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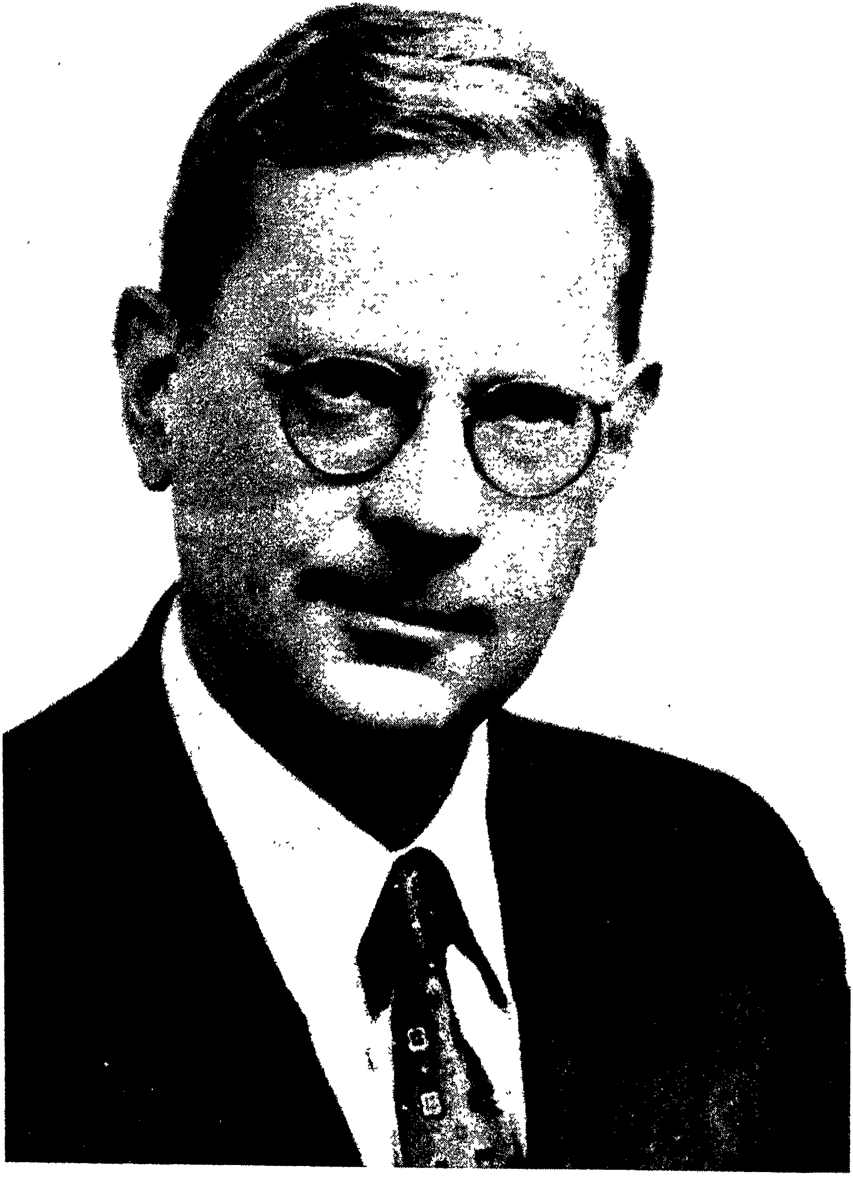

Dennis Robert Hoagland

Dennis Robert Hoagland

1884–1949

Dennis Robert Hoagland, professor of plant nutrition in the University of California, one of the most distinguished plant physiologists, and the world's leading authority on plant and soil interrelations, died in Oakland, California, September 5, 1949.

For more than 30 years, Professor Hoagland's life and work exerted a profound influence on the evolution of plant and soil science in America and abroad. But as with most great men, the totality of his achievement was greater than the sum of his impressive individual contributions. He personified the scientist with a broad outlook on his work and the world around him.

Hoagland graduated from Stanford University in 1907 and was elected that year to Phi Beta Kappa and to the Chemistry Honor Society, now Phi Lambda Upsilon. After graduation, he first elected to go on with work in chemistry at Stanford and, for one semester, was a graduate assistant in physical chemistry. In January of 1908, however, he became an instructor and assistant in the Laboratory of Animal Nutrition at the University of California. The new position brought him into professional contact with biology and took him to Berkeley, where, except for a few short gaps, he was to spend the rest of his life.

In 1910, Hoagland joined the Consulting Referee Board of Scientific Experts of the U. S. Department of Agriculture. This board was established to study the effect on health of various chemicals used in food processing and as preservatives, a question of national concern raised by the administration of the then recent Pure Food and Drug Act. He was associated with Alonzo Taylor in his work on the toxicity to humans of aluminum, copper, and sulfur compounds. His assignment took him to Philadelphia where he attended lectures as a graduate student in the University of Pennsylvania.

After completion of the work of the Referee Board in 1912, Hoagland accepted a graduate scholarship to work in animal biochemistry with E. V. McCollum in the Department of Agricultural Chemistry at the University of Wisconsin. In 1913 he received his master's degree with a thesis on "The influence of sodium benzoate on the synthesis of urea." In the same year he published with McCollum a series of three papers on the "Endogenous metabolism of the pig as modified by various factors." These publications are still quoted as authoritative statements on the processes involved.

Appointment in the Division of Agricultural Chemistry of the University of California in 1913 was a real opportunity to Hoagland. The department, under the leadership of John S. Burd, was chiefly interested in soil chemistry problems. Burd had the vision to encourage the search for principles rather than *ad hoc* solutions. By a fortunate circumstance Hoagland was also connected with the teaching program. It seems legitimate to speculate that the then large areas of ignorance in the field of plant and soil interrelations were sharply illuminated by penetrating questions from students.

The interruption of commerce in World War I focused attention on American dependence on German sources of potash fertilizers. The giant kelps of the Pacific Coast were suggested as a possible source of potassium. Hoagland undertook a systematic study of the inorganic and organic composition of kelps and reported his findings in three papers. His conclusions about the possibility of commercial exploitation of these organisms were not encouraging, but this research led him into a field of investigation in which he aquired a life-long interest and international renown: the accumulation of ions by plants. In 1915 he wrote in a paper dealing with the composition of kelps "Of far greater interest to the plant chemist and physiologist is the study of the chemical composition and metabolism of these remarkable plants [rather than that of their economic importance]. Their selective action on certain elements contained in sea water is very striking." He was particularly impressed with the remarkable ability of these plants to accumulate potassium and iodine in concentrations many times in excess of those found in sea water.

The second of Hoagland's early research activities concerned itself with the effect of hydrogen-ion concentration on plant growth. One of the accepted tenets of agricultural teaching in those days was that plants could grow well only at neutral or slightly alkaline reactions. It was with great surprise, therefore, that he discovered that barley plants made excellent growth in nutrient solutions at pH 5. It seemed that the chief importance of hydrogen ion was in relation to other ions rather than in its direct effect on the plant. To his orderly and critical mind it became clear that the complex problems of soil and plant interrelations must be studied by techniques which permitted rigid experimental control and the isolation of individual variables.

Hoagland gave expression to his convictions about the value of artificial culture methods in plant research by developing to a very high degree the water-culture technique for growing plants. He devised a culture solution to imitate a soil solution obtained from a soil of proved fertility. "Hoagland's solution" became a household term in laboratories of plant physiology throughout the world. The formulation of his culture solution was accompanied by a study of concentration versus total supply of ions, specific proportions of nutrients, and other basic concepts that underlie the use of nutrient solutions. He critically examined and rejected the idea of an "optimum nutrient solution," a point of view which was fully corroborated by later work.

After the organization of the new Division of Plant Nutrition, at the University of California at Berkeley, with Hoagland as head, he returned with renewed vigor to the problem that had attracted his attention in kelps—the absorption and accumulation of ions by plants. The quality of the immense contribution which he and his collaborators and associates made to this fundamental process of plant physiology can be judged only against a background of the ideas and concepts that prevailed when his work got under way. There was no clear view as to how inorganic elements are absorbed by plants. Discussions of this subject usually invoked such concepts as osmosis, permeability, and antagonism, none of which, as he later clearly demonstrated, could explain the absorption, accumulation, and retention against a concentration gradient of anions and cations by plant cells.

Hoagland opened the study of ion absorption by using intact barley plants. Promising as the early results were, he readily perceived the advantages of working with a unicellular organism from which relatively pure vacuolar sap could be obtained. At the suggestion of the late Nathaniel Gardner, he selected the fresh water alga, *Nitella*. This work clearly demonstrated that absorption of ions by plants is a metabolic process and not one of simple permeability. The accumulated ions were not precipitated in the sap but remained as free ions, the concentration of electrolytes in the *Nitella* sap being 25 times greater than that in the surrounding medium.

The next important phase of his researches on ion accumulation brought him closer to the system that was uppermost in his mind—the absorption of nutrients by the roots of higher plants. The broad outlines of a theory were already available from his previous work. What was needed was the formulation of an adequate experimental approach to the different system. He decided in the late 1920's that the most important prerequisite for future work was the development of a technique which would make available biological material of a definable and reproducible physiological status. Only in this manner could the various conflicting observations be resolved and a systematic effort directed toward the elucidation of factors underlying salt absorption by roots.

Hoagland concluded that the fundamental questions of ion absorption by root cells can be studied most effectively by eliminating, during a brief experimental period, the complications of shoot and root relationships. He concentrated, therefore, on excised roots obtained from plants grown under experimental conditions designed to yield, subsequent to the removal of shoots, root systems with a high capacity for salt absorption. Among the essential conditions for a high capacity for ion absorption by roots were a low salt and a high carbohydrate status. Under these conditions the excised roots were found to be "the most active salt-accumulating system so far [1936] investigated."

Once the tedious but indispensable job of evolving a suitable physiological technique was completed, progress was rapid and gratifying. An impressive array of data was amassed over the years on the influence of temperature, light, hydrogen-ion concentration, ion selectivity, concentration of anions and cations, differences in rates of absorption, and the effect of one ion on the absorption of another ion of the same or opposite charge. A striking correlation was obtained between the supply of oxygen and the absorption of salts by roots against a concentration gradient. A solid scientific foundation was thus laid for the understanding of the importance of aeration in soils and for the interpretation and prediction of a multiplicity of plant responses to fertilization treatments, and other chemical changes in the soil.

The final phase of his investigations on absorption of ions occurred just before and during World War II. With excised barley roots he studied the effect of reversing the external concentration gradient on ion entry and the influence of inhibitors on ion accumulation. He also returned to *Nitella*, this time employing radioactive isotopes. The technique permitted separation of the two stages of ion absorption by cells: from the external medium into the cytoplasm, and from the cytoplasm into the vacuole. The fundamental conclusion, which he and his colleagues had reached almost two decades earlier, that ion accumulation is a metabolically linked process, was confirmed. By the use of radioisotopes in the late 1930's, he showed that ions first accumulate in the cytoplasm and then migrate to the vacuole by a process akin to secretion until the vacuolar concentration becomes higher than that in the cytoplasm and decidedly higher than that of the external dilute solution.

Hoagland's own work on problems of soil chemistry, insofar as it affects the nutrition of crops grown in the field, was especially concerned with zinc, potassium, and phosphorus deficiencies of fruit trees in California. In this he entered, in the late 1920's, into a harmonious cooperation with W. H. Chandler of the Pomology Division. In a concerted attack on a complex problem, each division contributed what it was best equipped and qualified to do. The result of this collaboration was the clear identification of "little leaf" of fruit trees as a zinc deficiency and its reproduction under controlled greenhouse conditions. The importance of these studies to California agriculture is shown in the fact that zinc is now second only to nitrogen in importance as a fertilizer element for orchard crops. The investigation of potassium nutrition of fruit trees had a bearing on "prune dieback," another nutritional disease of fruit trees in California. An intensive chemical investigation followed into the question of potassium absorption in relation to replaceable, nonreplaceable, and soil-solution potassium. His interest in the nutrition of fruit trees continued, and in 1940 he produced, under controlled conditions, the first molybdenum-deficiency symptoms in fruit trees. It was also under his influence and encouragement that intensive studies into other aspects of micronutrients were undertaken in the Division of Plant Nutrition.

In his personal relationships, Hoagland's chief characteristic was his integrity and objectivity of outlook. He was a scientist who carried the scientific mode of thinking outside his own specialty. In the 17 years during which the writer was associated with him as a student, colleague, and friend, he never heard him once discuss a person or an issue, scientific or otherwise, except in an objective manner. He approached his students with confidence and good will, always crediting them at the start with ability and industry.

He was an ideal collaborator in scientific research, never seeking dominance for his own point of view but always inviting a free flow of ideas. He was meticulous in giving credit where credit was due and was generous in acknowledging the contributions of his associates. He was a master of clear exposition and had a real feeling for style. Although writing came to him easily, he always preferred to defer publication of results until the evidence was carefully assembled and checked.

It was only natural that Hoagland's accomplishments, his qualities of mind and character, gained him wide recognition and many honors. His counsel was sought and valued within his own university, to which he gave unstintingly of time and effort in many arduous administrative assignments, usually at the expense of his own leisure and in later years at the expense of his health. In 1934 he was elected a member of the National Academy of Sciences. The American Society of Plant Physiologists, which was his closest scientific affiliation, bestowed upon him its highest honor by granting him in 1929, the first Stephen Hales Award in recognition of his outstanding research contributions. He was also elected president of the society and occupied other important offices in it.

The high esteem in which he was held by plant physiologists throughout the world is attested by his recent appointment as president of the Section of Plant Physiology at the forthcoming VIIth International Botanical Congress to be held in Sweden in 1950. Unfortunately, poor health forced him to decline this international honor.

Many other socieities in which he held membership honored him by election to presidency: Western Society of Soil Science (1924); Western Society of Naturalists (1931); Botanical Society of America, Pacific Division (1929); American Association for the Advancement of Science, Pacific Division (1941). He served as consulting editor for SOIL SCIENCE, American Journal of Botany, and Plant Physiology. He took a prominent part in the organization of the Annual Review of Biochemistry, serving from its inception on the advisory board and later on the board of directors. He was a member of the board of collaborators for the U. S. Department of Agriculture Salinity Laboratory at Riverside, California, and the Soil, Plant, and Animal Nutrition Laboratory at Cornell University.

In 1940, the American Association for the Advancement of Science awarded him a $1,000 prize for an outstanding paper presented at the Philadelphia meetings. In 1942 he was invited by Harvard University to give the John M. Prather lectures. The lectures were later published in book form, and constitute the only book which he found leisure to prepare.

His own colleagues in the various faculties bestowed upon him the highest honor within the university by appointing him in 1942 Faculty Research Lecturer.

In 1920, Hoagland married Jessie A. Smiley, who died suddenly of pneumonia in 1933. Her death left him the responsibility of bringing up three sons who, with his mother and a brother, survive him.

The scientific influence of Professor Hoagland's life has not come to an end with his death, but will continue through the deep impression he has made on the minds and hearts of his many students and friends.

DANIEL I. ARNON

EFFECTS OF ENERGY PROPERTIES OF SOME PLANT NUTRIENTS ON AVAILABILITY, ON RATE OF ABSORPTION, AND ON INTENSITY OF CERTAIN OXIDATION-REDUCTION REACTIONS[1]

H. P. COOPER

South Carolina Agricultural Experiment Station

Received for publication March 28, 1949

EDITORIAL NOTE

In the March, 1948, issue of the *Journal of the Australian Institute of Agricultural Research*, an article on "The Need for Destructive Criticism" drew special attention to H. P. Cooper's concepts "on the order in which plants absorb elements from the soil." The author of this article said that "the whole of this theory is plain rubbish." He concluded with a plea that scientists "tackle the editors who allow bad work to pass."

Since several of Cooper's articles had appeared in SOIL SCIENCE, this criticism was brought to the attention of the consulting editors of our journal who were in best position to evaluate Cooper's concepts.

While awaiting replies to these letters, the editor of SOIL SCIENCE received a new paper from Cooper on "Effects of Energy Properties of Some Plant Nutrients on Availability, on Rate of Absorption, and on Intensity of Certain Oxidation-Reduction Reactions." This provided an excellent opportunity for a systematic review of Cooper's work. So the paper was submitted, for comment, to a number of our best-trained physical chemists in soils, both here and abroad.

In due time, 16 single-spaced typewritten pages of comment on his concepts, in general, and on his latest paper, in particular, were assembled and forwarded to Cooper for his consideration. Almost without exception, the reviewers questioned the validity of his theories and expressed doubt concerning the desirability of publishing the paper.

But two of them thought differently. One wrote: "In view of the fact that the author has been subjected to open criticism, I think it would be best if the paper could be published. The theories which he expounds have now attracted attention and will probably be subjected to critical examination and useful discussion, and this invariably leads to progress. In my opinion, it is not so much the *few* speculative and controversial papers we should discourage—for they, at least, contain some thoughts and will, even if erroneous, often lead to new truths—but the *many* papers in which there is perhaps nothing to criticize but which have nothing but some inconclusive experimental data to offer."

A second very capable reviewer wrote:

"I cannot see that there is much wrong with Cooper's view. We do not know the enormous influence of H ions in modifying the physicochemical processes going on in the soil. Then why not the other ions? And if Cooper says 'look for the ionic activity,' why should the editor of SOIL SCIENCE turn his back because there are people who do not care to understand the difference between the metallic and the ionic state. I have not read any of Cooper's other papers, but about this particular paper my frank opinion is that it is a good piece of work, insofar as it emphasizes the importance of ionic equilibrium and activity concepts. We know so little about the way plants make use of the nutrient materials that any pointers toward the solution of that highly important problem should be welcome."

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[1] Technical Contribution No. 160—South Carolina Agricultural Experiment Station, Clemson, S. C.

On receipt of the extended comments on his concepts and on his current paper, Cooper wrote a very interesting and instructive rebuttal that dealt with the several issues, point by point. The editor was so impressed by the author's carefully worded comments and by his calm assurance that he decided to accept the paper for publication.

FIRMAN E. BEAR

One of the major differences in the properties of mineral nutrients and of organic compounds synthesized by plants is the potential energy stored in the organic compounds as a result of absorption of light energy in photosynthetic reactions. Since animals depend largely upon organic compounds for growth energy, it is desirable to consider the energy properties of the mineral nutrients utilized by plants in synthesizing the organic compounds.

The relation of the energy properties of nutrient compounds to soil fertility problems and plant nutrition has been presented in several previous papers (8 to 20). It is appropriate also to consider factors that would be logically related to the energy reactions occurring in the nutrition of plants and animals. Some of the significant factors are as follows: (*a*) relation of relative strength of ions to intensity of absorption of certain nutrients by plants, (*b*) effect of phylogenetic characteristics upon the nutrient content of plants, (*c*) phylogenetic tolerance mechanisms such as occur in selective accumulation and in selective exclusion of nutrients by certain plants, (*d*) conditions favoring production of proteinaceous and carbonaceous plants, (*e*) relation of exothermic and endothermic reactions to the nutrition of organisms, (*f*) quality of energy in sunlight, (*g*) quality of energy absorbed by chlorophyll, and (*h*) quality of energy required in the assimilation of some anions. A comprehensive study of the nutrition of plants and animals will require careful consideration and determination of the correlation and interrelation of these factors in various nutritional complexes.

ENERGY PROPERTIES OF NUTRIENTS

A consideration of the energy properties of nutrient ions utilized by plants may be of great value in interpreting some significant nutritional problems. The Law of the Photochemical Equivalent has been utilized in correlating all energy values and relationships included in this paper. In considering the application of this law to plant nutrition, it is particularly desirable to note the multiplicity of biochemical growth mechanisms characteristic of various groups of plants. The existence of such mechanisms makes possible vegetative cover, where environmental conditions are suitable, for virtually all existing soil nutritional complexes. It is necessary, therefore, to consider the average chemical composition of a large variety of plants with widely different nutrient requirements, grown over a wide range of soil and climatic conditions, to illustrate the relation between the energy properties of nutrient compounds and the intensity of absorption and utilization of various nutrients by plants.

Every form of energy may be considered as compounded of two factors: the capacity factor and the intensity factor. These factors may be expressed, respectively, as follows: mass of water and difference of level, thermal capacity and temperature, volume and pressure of gas, titrable acidity and pH value. Since the intensity factor of acidity of which the pH value is a convenient measure, has been very useful in biological studies, it seems desirable to consider the relative intensity factor of energy of nutrients other than H. As there is no comparable method of easily determining the intensity value of other ions in a nutritional medium, it may be useful to consider the relative intensity factors involved in ion formation. One of the most satisfactory measures of the intensity factor of ion formation is the standard oxidation-reduction potentials in table1. It may not be possible in many situations to make direct use of such values in quantitative studies, but qualitatively this ion series is a very satisfactory guide. Most of the standard electrode potentials utilized in these studies were reported by Kolthoff and Furman (32), the International Critical Tables (31), and Hodgman (29). The electrode potentials reported by different authors for such elements as Ca and Mg differ widely. The order in this grouping is very probably according to the relative strength of ions. For some of the complex anions, the decomposition voltage or the discharge potential of aqueous solutions of acids on platinum electrodes is included. The overvoltage value, which is the difference between the potential of the electrode at which gas evolution occurs and the theoretical reversible oxidation-reduction potential for the same solution, should be considered in evaluating the significance of the decomposition voltages in comparison with standard oxidation-reduction potentials. Cooper *et al.* (8 to 20) have pointed out that most biological reactions are more definitely related to the intensity factor of energy than to the capacity factor. The intensity factor of energy in ion formation is of primary importance in considering both the intensity of removal of cations from soil colloids by electrodialysis and the intensity of absorption of certain nutrient cations by plants (13, 15). The two standard measures of the intensity factor in ion formation likely to be of greatest value in biological studies are the standard electrode potentials and the ionization potentials (18, 19).

Significance of ionization potentials

Ionization potentials should give one of the most accurate and significant ion series, since the values determined, unlike standard electrode potentials, are probably not significantly affected by concentration and energy of hydration. Certain ionization potentials of elements in various stages of ionization reported by Millikan and Bowen (41), Noyes and Beckman (44), Latimer and Hildebrand (33), and Hodgman (29) are included in table 2. The equivalent energy, expressed in volts required for removal of last bound electron, is shown in the second column. This arrangement gives very little information on the relative activity of different ions except the monovalent ions of the alkali metals and H. The equivalent voltage values in the fourth column give a more satisfactory ion series, or a better grouping of the relative activity of the ions in their most common atomic ionic valence state in some nutrient media. An atomic ionic series, arranged according to the relative strength of ions from the strongest to the weakest, is Cs, Rb, K, Na,

TABLE 1

Standard oxidation-reduction potentials of some nutrient elements at 25°C. on the hydrogen scale

The sign of the potential is opposite that on the electrode

	CHARGE ON ION	ELECTROMOTIVE FORCE *volts*
	Cations (+)	
Potassium	K^+	+2.92
Sodium	Na^+	+2.71
Calcium	Ca^{++}	+2.50
Magnesium	Mg^{++}	+1.55
Aluminum	Al^{+++}	+1.30
Manganese	Mn^{++}	+1.10
Zinc	Zn^{++}	+0.76
Chromium	Cr^{++}	+0.56
Gallium	Ga^{+++}	+0.50
Iron	Fe^{++}	+0.44
Cadmium	Cd^{++}	+0.40
Cobalt	Co^{++}	+0.29
Nickel	Ni^{++}	+0.22
Tin	Sn^{++}	+0.13
Iron	Fe^{+++}	+0.04
Hydrogen	H^+	±0.00
Antimony	Sb^{++}	−0.10
Arsenic	As^{++}	−0.29
Copper	Cu^{++}	−0.34
Mercury	Hg^{++}	−0.80
Platinum	Pt^{++}	−0.80
Gold	Au^+	−1.50
	Anions (−)	
Hydroxyl	OH^-	−0.41
Silicon	$HSiO_3^-$	....
Boron	$H_2BO_3^-$	....
Selenium	$HSeSO_4^-$	....
Iodine	I^-	−0.55
Sulfur	S^{--}	−0.55
Oxalate	$HC_2O_4^-$	−0.95
Bromine	Br^-	−1.08
Water	O_2	−1.23*
Chlorine	Cl^-	−1.36
Chlorate	ClO_3^-	−1.44
Acetate	CH_3COO^-	−1.57
Nitrate	NO_3^-	−1.69†
Sulfate	HSO_4^-	−1.69†
Phosphate	$H_2PO_4^-$	−1.70†
Oxygen	O^{--}	−1.90
Fluorine	F^-	−1.96

* The decomposition voltage of water in a hydrogen-oxygen cell.

† Discharge potential of acid on platinum electrode, overvoltage effect.

Li, Ba, Sr, Ca, H, Mg, Mn, Fe, Co, Zn, Be, and Cu. In this grouping the H ion ranks next to Ca, and in comparable concentrations it would be expected to predominate over any other ion lower in the series. This grouping is in agreement with the recognized order of activity of certain cations in soil colloidal studies.

The ionization potential values in table 2 and the solubility values in table 3 suggest that in absence of such strong anions as Cl^-, CH_3COO^-, HSO_4^-, and NO_3^-, the elements below H in the fourth column (table 2) would be expected to form complex ions and would not be present in large amounts in atomic form in soil solutions. These ionization values also suggest some of the reasons why it is not possible to remove large quantities of elements below H in this series by electrodialysis. Some of the elements below H, however, can be readily extracted from the soil by addition of relatively strong anions which form soluble compounds with the different metallic elements. It is not likely that an element like Al, with an inmost normal valence ionization potential of 28.31 volts, would form a significant quantity of atomic ions in the soil solution. The solubility and removal of such an element from the soil would very probably be determined by the relative quantity of the strong anions in the soil solution capable of forming soluble compounds.

TABLE 2

Approximate ionization potentials required for removal of valence electrons from certain plant nutrients in the atomic state

REMOVAL OF LAST BOUND ELECTRON		REMOVAL OF INMOST COMMON VALENCE ELECTRON	
Element	Equivalent Volts	Element	Equivalent Volts
Cs^+	3.87	Cs^+	3.87
Rb^+	4.16	Rb^+	4.16
K^+	4.32	K^+	4.32
Na^+	5.12	Na^+	5.12
Ba^+	5.19	Li^+	5.36
Li^+	5.36	Ba^{++}	9.95
Sr^+	5.67	Sr^{++}	10.98
Al^+	5.96	Ca^{++}	11.82
Ca^+	6.09	H^+	13.53
Mn^+	7.41	Mg^{++}	14.96
Mg^+	7.61	Mn^{++}	15.70
Cu^+	7.68	Fe^+	16.16
Co^+	7.81	Co^{++}	17.30
Fe^+	7.83	Zn^{++}	17.89
Be^+	9.28	Be^{++}	18.12
Zn^+	9.36	Cu^{++}	20.34
H^+	13.53	*Al^{+++}	28.31

* The energy required to remove second valence electron to form Al^{++} = 18.74 volts.

Significance of solubility of nutrient compounds

In comparing the relative strength and activity of ions in any nutritional complex, comparable concentrations must be considered, as mass action resulting from high concentrations of ions may become a more significant factor than relative strength of ions in certain situations. This makes it desirable to consider the solubility values of the different nutrient compounds and the probable effect of these values on the concentration of the different nutrient ions in the soil solution and in the plant. The solubility of different nutrient compounds varies widely. Since the solubility data reported in standard reference works have been determined by different investigators under different temperatures, close comparison is not possible. Solubility values of different nutrient compounds in grams per 100 ml. of cold water are shown in table 3. Solubility of the alkali metal compounds and of the alkaline earth metal compounds varies widely.

The relatively low solubility of most of the Ca compounds suggests one of the reasons for the generally recognized fact that many soils relatively high in Ca are classified among the most productive. The low solubility of virtually all the Ca compounds listed, except the NO_3 and Cl, would result in accumulation of the insoluble Ca compounds in the soil. The relatively high OH-ion concentration commonly accompanying a relatively high Ca-ion concentration in the soil solution would tend to conserve such minor plant nutrients as Mn, Zn, Fe, Co, and Cu, in complex hydroxyl compounds in many soils. Under such conditions certain of these minor nutrients may enter into very low solubility compounds and become relatively unavailable to many plants.

TABLE 3

Solubility of certain nutrient compounds*

In grams of anhydride per 100 gm. cold water. Temperature around 30° or 0°C., as indicated

ION	HCO_3	CO_3	C_2O_4	OH	SiO_2	PO_4	HPO_4	H_2PO_4	SO_4	NO_3	Cl
K........	22.4	112.0	33.0	97.0^{0}	s.	sl.s.	v.s.	33.0	12.0	31.6	34.7
Na.......	6.9^{0}	7.1^{0}	3.7	109.0	s.	28.3	21.9	110.3	19.5^{0}	73.0^{0}	35.7^{0}
NH_4......	11.9^{0}	100.0	4.0	42.0	....	....	42.9^{0}	22.7^{0}	70.60^{0}	118.3^{0}	29.7^{0}
Ca........	....	0.0014	0.00067	0.185^{0}	0.0095	0.002	0.02	1.8	0.298	102.0^{0}	59.5^{0}
Mg.......	....	0.0106	0.07	0.0009	....	0.02	0.31	....	26.0^{0}	42.33	35.3
Al........	....	....	i	0.00015^{20}	sl.s.	i	....	....	31.3	63.7	69.9^{15}
Mn.......	....	0.0065	0.03	0.0002	i	....	. ..	. ..	52.0	426.4^{0}	62.2
Zn........	....	0.001	0.00079	0.00000026	i	i	i	i	86.5^{80}	327.3^{40}	432.0
Fe........	....	0.0067	0.022	0.00067	....	....	....	....	15.65	83.5	64.4
Co........	....	i	i	0.00032	....	i	....	. ..	36.2	133.8^{0}	45.0^{7}
Cu.......	....	i	0.0025	i	....	i	i	i	14.3^{0}	137.8^{0}	70.6^{0}

* s = soluble, v = very, sl = slightly, i = insoluble.

The high solubility of K_2CO_3, Na_2CO_3, and $(NH_4)_2CO_3$, as compared with the relatively low solubility of $CaCO_3$, may be a very significant factor in determining the relative quantity of CO_2 available to plants for the synthesis of organic compounds in different nutrient media. The predominance of Ca in a nutrient medium may favor accumulation in the plant of $CaCO_3$ and certain other low-solubility Ca compounds resulting from organic acids such as oxalates, malates, tartrates, and citrates; whereas the predominance of K, Na, or NH_4, or a combination of these, would create a favorable condition for maintaining a relatively large supply of CO_2 available for synthesis of organic compounds. The importance of these relationships in nutrition suggests the desirability of considering some of the possible mechanisms influencing the relative quantity of N and C compounds available in plants for synthesis of complex organic compounds, which may largely determine whether the food products synthesized by different plants will be classified as proteinaceous or carbonaceous products.

Relation of standard electrode potentials to intensity of removal of cations from soil in electrodialysis studies

In using such values as standard electrode potentials in soil fertility and plant nutrition studies it is particularly desirable to consider comparable concentrations, as mass action accompanying high concentrations may mask the relative effect of strength of ions. Where comparable or known concentrations are considered, it will be easier to determine the relative significance of the different ions in nutritional media.

Cooper and Paden (13), have reported a very close correlation between the intensity of removal of cations by electrodialysis from soil colloidal complexes and the standard electrode potentials. The intensity of removal of K, Na, Ca, and Mg from a composite soil sample in the first 2-hour period, expressed as percentage of the total quantity of each cation removed in 32 hours, was 56.00, 24.66, 17.49, and 11.98 respectively. The intensity of removal of the cations Rb, K, Na, Li, Ca, and Mg in fractional electrodialysis from homionic soil colloids, expressed as percentage of the total amount extracted in the first 2-hour period, was 91.32, 60.51, 53.43, 43.15, 36.89, and 24.31, respectively. These data clearly illustrate the relation between the relative strength of certain ions and the intensity of their removal from soils by electrodialysis.

The relative solubility of the hydroxides of the metals (table 3) may also be an important factor in determining the relative quantity of the metals removed by electrodialysis as compared with the amount removed by extraction solutions such as acetates, chlorides, nitrates, and sulfates containing anions which form soluble salts of the different metals.

Intensity of removal of cations from plant tissue by electrodialysis

The intensity of absorption of nutrient ions by many crop plants would be expected to be correlated with the intensity of removal of the different cations from the soil by electrodialysis. It is well known that certain plants differ markedly in the ions selectively absorbed. Because of the variety of conditions involved, such as permeability of root membrane, utilization of ion, and formation of insoluble compounds in the plant, it is very difficult to determine the order of intensity of absorption of ions by different plants. It is believed, however, that fractional electrodialysis studies of plant tissues will serve to establish the general relationship between the relative strength of ions, as measured by electrode and ionization potentials, and their intensity of absorption, mobility in plant tissue, and utilization by certain plants.

To determine the intensity of removal of cations, fresh samples of cotton, corn, and soybean tissue were electrodialyzed for 29 to 32 hours. The diffusate was collected at successive intervals, and the amount of materials removed at each extraction period was determined by Cooper, Paden, and Smith (15). The percentage of the various metals removed at each extraction period shows that there is a wide differential in the intensity of removal of cations from plant tissue.

The relation between the relative strength of ions and the intensity of removal of cations is illustrated by the percentage of total K, Na, Ca, and Mg extracted from cotton tissue during the first hour: 91.40, 49.57, 31.10, and 1.60, respectively. During the 3–5-hour extraction period, these quantitative relationships were reversed; the percentage then was 0.50, 5.18, 11.90, and 60.20, respectively. Likewise, the percentage of total K, Na, Ca, and Mg extracted from corn tissue during the first ¼-hour period was 81.55, 22.23, 13.19, and 2.25, respectively. A similar relationship for soybean tissue was found in the first extraction period with a percentage removal of the metals of 43.09, 36.47, 1.73, and 1.46, respectively.

The data from fractional electrodialysis studies of both plant tissue and soils show the same order of intensity of removal of cations. Establishment and general recognition of the significance of the correlation between oxidation-reduction potential values, ionization potential values, and intensity of removal of cations from soil and plant tissue can be of very great assistance in solving many significant problems in soil fertility and plant nutrition.

RELATION OF RELATIVE STRENGTH OF IONS TO INTENSITY OF ABSORPTION OF CERTAIN NUTRIENTS

As some plants apparently tend to absorb nutrient ions selectively according to relative strength of ions as expressed in electrode potentials rather than according to the concentration of ions in the nutrient medium, it is possible to predict qualitatively the probable relative quantity of ions of different strengths that may be absorbed by many plants. Where comparable concentrations of nutrients are present in the medium, the expected average quantity of materials in a large variety of plants would be in agreement with the relative strength of ions. The original data utilized in developing the interpretations discussed in this paper were reported by the following investigators: Hoagland and his associates (28) Reed and Haas (49), Bear and Prince (1), Osterhout (47, 48), Beeson (2, 3), Collander (7), Wallace *et al.* (59), Goldschmidt (26), Snider (55), Newton (43), and Cooper and Blink (21). Plants or tissues that tend selectively to accumulate relatively large quantities of certain nutrients and exclude others may be considered an exception to this generalization. The mineral composition of Florida-grown vegetables reported by Sims and Volk (54) shows that the mineral content of plants is apparently much more closely correlated with the relative strength of ions than with concentration of ions as expressed in pounds of exchangeable cations per acre. The chemical composition of pasture herbage reported by Blaser *et al.* (4) and data reported by Cooper *et al.* (20) can be interpreted to show the relation between the relative strength of ions and the nutrient content of plants.

Plant nutrient elements arranged in order of relative strength of ions from the strongest cation material to some of the stronger anion materials are included in table 4. The data in this table represent averages for a large number of chemical analyses of plants grown under varying conditions. This type of information may not be applicable to many specific situations, but it will serve to illustrate some of the most common nutrients utilized by many plants. The metallic nutrients are arranged according to the standard electrode potential and the discharge potential, or decomposition voltage of aqueous solutions of acids on platinum electrodes, as reported in previous papers by Cooper *et al.* (15 to 20). The different elements are expressed as percentages of the plant and as milliequivalents. Under the percentage values the elements are expressed as percentage of K, and under the milliequivalent values the elements are expressed as percentage of N.

TABLE 4

Average chemical analyses of a large number of plants with the arrangement of metallic nutrient elements in order of standard electrode potentials or the relative strength of their ions from the stronger cations to the stronger anion materials

ARRANGEMENT OF NUTRIENTS IN ORDER OF STRENGTH OF IONS			AVERAGE CHEMICAL COMPOSITION OF A WIDE VARIETY OF PLANTS			
Material	Ion	Standard electrode potential	Per cent of		Milliequivalents	
			Plant	K	Per 100 gm. of plant	Per cent of N
Potassium	K^+	+2.92	1.61	100.00	41.18	8.90
Sodium	Na^+	+2.71	0.25	15.53	10.87	2.35
Calcium	Ca^{++}	+2.50	0.76	47.20	37.92	8.20
Magnesium	Mg^{++}	+1.55	0.27	16.77	22.20	4.80
Manganese	Mn^{++}	+1.10	0.018	1.12	0.66	0.14
Iron	Fe^{++}	+0.43	0.018	1.12	0.65	0.14
Silicon	....	....	0.65	40.37	92.66	20.03
Sulfur	HSO_4^-	−1.69*	0.26	16.15	16.22	3.51
Phosphorus	$H_2PO_4^-$	−1.70*	0.25	15.53	24.21	5.23
Chlorine	Cl^-	−1.36	0.64	39.75	18.05	3.90
Nitrogen	NO_3^-	−1.69*	2.16	134.16	462.53	100.00

* The discharge potential or decomposition voltage of aqueous solutions of acids on platinum electrodes.

Analyses of 1,016 plant samples representing a wide variety of crops (table 4) show a close correlation between the relative strength of some ions and the average content of the different nutrients in plants. Average values may be useful in presenting a general trend but will not be representative for different types of crop plants. Most of these analyses represent plants grown on humid climate soils, which usually contain a relatively low concentration of Na ions and a relatively high content of Fe. It is noted that the Na content of plants is relatively low as compared with the relative strength of the Na ion. This is very probably partly due to the ability of some plants, through a Na-tolerance mechanism, selectively to exclude Na and to the relatively low concentration of Na ions in most humid climate soils. The relatively high content of Na in cotton, potatoes, and carpet grass shown in table 5 indicates that certain plants, particularly those fertilized with $NaNO_3$, may absorb a relatively large quantity of the available Na in the soil solution of humid soils. It is well known that there is a wide differential in the selective uptake of ions by different plants grown in the same nutrient solution. Certain members of the chenopodiaceae family (including mangels and beets), asparagus, mustard, and halicystis may contain a large amount of Na (7,28). Table 5 shows that the Fe content reported for some plants is relatively high. In certain cases this may be due to adherence of Fe to the surface of the plants. The high content of Fe in most humid soils as compared with the other minor nutrients may be an important factor in increasing the relative concentration of Fe in the soil and significantly increasing the relative amount of Fe absorbed by many plants. The apparent exceptions noted for Na and Fe emphasize the significance of considering such factors as the inherent characteristics of the plant, such as the selective accumulation or the selective exclusion of elements, the solubilities and the relative concentrations of the different ions in the nutrient media, in addition to the relative strength of ions, in determining the initial intensity of absorption of ions and the nutrient content of plants. The relative strength of ions as a factor in determining the intensity of absorption of nutrients by plants should be considered on the basis of comparable concentrations in the nutrient media. These relationships make it desirable to consider some of the important characteristics of plants which influence their nutrient requirements and chemical composition.

Need for balanced fertilizer program

The large number of elements that may be found in plants, as shown in tables 1 and 4, suggests the desirability of considering complete nutrient complexes in our fertilizer program. The three nutrients N, P, and K are not adequate for many of the humid climate soils heavily fertilized for production of fruits, vegetables, and other crops of high acreage value. The selective absorption or the selective exclusion of certain nutrients by different plants makes desirable the inclusion of a differential in the combination of nutrients in the fertilizer for different crop plants. Excessive quantities of the stronger nutrient ions may result in selective absorption of the stronger ions by many plants, tending to limit absorption of the weaker ions with the same ionic charge. Only small quantities of many of the minor nutrients are required for normal growth of most plants. The relatively low solubility of certain minor nutrient compounds and the relatively low intensity of absorption of the weaker nutrient ions call for a thorough understanding of the function and of the relative intensity of absorption of the different plant nutrients.

Certain functions of different plant nutrients

It is widely accepted that plants obtain much of their nutrient supply in ionic form. According to the theory of ionic absorption, it is logical to assume that the major absorption system in plants is largely determined by the capacity to absorb positively charged and negatively charged materials. If it is assumed that nutrient absorption is primarily based upon the capacity of plants to absorb a positive or a negative charge, it might be expected that the differential in the intensity of absorption of nutrient ions would be related to the relative strength of the different ions. Summary data reported by Wallace *et al.* (60) on the approximate constant cation-anion ratio in some plants definitely suggest the significance of the ionic absorption theory and the necessity for a cation-anion balance in plant nutrition. Induced cation and anion deficiencies may be expected according to the theory of cation-anion competition, particularly in unbalanced nutrient media.

Following are some of the specific functions influencing the relative quantity of the different nutrients absorbed by plants:

Certain nutrients have a specific structural function as a component part of organic compounds.

Some nutrients may influence certain oxidation-reduction reactions at specific energy levels or may be acceptors or donors of specific quanta of energy at characteristic energy levels.

The primary function of certain nutrients may be the maintenance of an ionic balance in plant tissues. Such nutrients might be expected to accumulate in the roots and stems.

Certain nutrients affect solubility, mobility, and availability of such substances as CO_2, organic acids, and other organic compounds in the plant.

Removal of excessive soluble ions or compounds from plant tissue in the form of insoluble materials may be one of the primary functions of some nutrients.

EFFECT OF PHYLOGENETIC CHARACTERISTICS ON NUTRIENT CONTENT OF PLANTS

To illustrate the effect of certain characteristics of some crop plants upon their nutrient contents, the chemical compositions of selected crop plants grown under comparable conditions are shown in table 5. Numerous investigators, as reported by Miller (40), have noted the differential in the chemical composition of plants grown in the same or similar nutrient media. These findings have focused attention on the characteristics of certain crop plants which may affect their chemical composition or nutrient content, since the nutrient contents vary widely from the average values for a large number of plants. Cotton, okra, sweet potatoes, and plants in the nightshade family, such as tomatoes and potatoes, apparently accumulate Ca in larger quantities than might be expected from the relative strength of the Ca ion. These plants have a chemical composition similar to that of leguminous plants. Many plants that are relatively high in Ca may be relatively high in Cl and relatively low in Si. Wheat straw is relatively low in Ca and high in K and Si. Wheat seed, in common with most seed and other reproductive tissue, is relatively low in Ca and Cl and high in Mg, P, and N (19).

PHYLOGENETIC TOLERANCE MECHANISMS IN PLANTS

Most of the crop plants now grown in forested areas originated in a habitat supporting chiefly a grass or herbaceous vegetation. Extension of the culture of certain crop plants beyond the regions with optimum physiological growth factors makes it desirable to give special consideration to some of the physiological growth requirements of different crops grown under varying conditions. In considering the optimum habitat for different crop plants, special attention has been given to requirements for successful growth. Existence of plant growth on virtually every normal or mature soil where sufficient moisture is available suggests that in many situations plants may be subjected to excessive quantities of certain nutrients rather than to deficiencies. It is logical to assume that the more or less fixed phylogenetic characteristics of plants have been largely determined by a

TABLE 5

Average chemical composition of crop plants grown under comparable conditions

Metallic nutrients are arranged according to relative strength of ions as indicated by normal electrode potentials

CROP	NUMBER OF SAMPLES	ELEMENTS ARRANGED IN ORDER OF ELECTROLYTIC SOLUTION PRESSURE OR INTENSITY OF ION FORMATION												
		K	Na	Ca	Mg	Al	Mn	Fe	Si	S	P	Cl	N	Ash
		Standard electrode potentials of metals in equivalent volts												
		+2.92	+2.71	+2.50	+1.55	+1.30	+1.10	+0.43	....	−1.69*	−1.70*	−1.36	−1.69*	....
		Per cent of different nutrient elements in dry matter of plant												
Cotton plant	28	0.83	0.45	1.70	0.45	0.040	0.030	0.056	0.09	0.28	0.24	0.75	1.91	9.00
Cotton seed	10	1.20	0.31	0.15	0.35	....	0.001	0.005	....	0.26	0.23	....	3.96	....
Okra plant	1	0.61	0.02	1.75	0.18	....	0.013	0.043	0.41	0.27	0.24	0.63	2.35	....
Okra seed	1	0.52	0.03	0.17	0.20	....	0.003	0.021	0.08	0.29	0.27	0.04	5.07	....
Sweet potato vines	2	2.50	0.60	1.14	0.50	0.280	0.009	0.027	0.48	0.26	0.17	0.64	2.00	....
Sweet potato roots	2	1.60	0.72	0.10	0.08	0.080	0.001	0.005	0.003	0.03	0.19	0.31	0.72	....
Tobacco leaf	1	2.69	0.03	2.42	0.62	0.011	0.057	0.024	1.06	0.31	0.27	1.31	2.57	11.53
Tobacco stem	1	1.90	0.05	0.56	0.25	0.004	0.017	0.009	0.56	0.18	0.14	0.99	1.18	5.31
Tomato vine	1	3.68	....	3.48	0.44	....	0.024	0.016	....	0.28	0.32	....	1.80	....
Tomato fruit	1	5.24	0.26	0.29	0.29	....	0.004	0.005	....	....	0.51	...	4.51	....
Potato plant	16	1.62	0.50	4.12	1.15	....	0.010	....	....	0.68	0.26	2.25	....	....
Potato tuber	315+	2.28	0.10	0.05	0.13	....	0.002	0.011	....	0.12	0.25	0.29	1.67	....
Pepper plants	2	1.20	0.04	1.42	0.39	....	....	....	0.04	0.49	0.15	0.85	2.56	....
Pepper pods	2	0.95	0.03	0.10	0.09	....	...	....	0.21	0.32	0.26	0.36	2.34	....
Wheat straw	8	1.01	0.13	0.13	0.08	0.010	0.066	0.009	1.01	0.15	0.11	0.51	0.53	4.43
Wheat seed	8	0.40	0.11	0.04	0.15	0.005	0.048	0.004	0.35	0.16	0.43	0.10	1.72	1.96
Legumes‡	274	1.13	....	1.47	0.38	....	0.012	0.015	....	....	0.18	....	2.38	....
Grasses & cereals‡	320	1.54	....	0.33	0.21	....	0.014	0.011	....	....	0.14	....	0.99	....
Carpet grass	11	0.71	0.51	0.32	0.21	0.012	0.013	0.030	0.82	0.18	0.17	0.47	1.27	7.08
Kentucky bluegrass	9	1.96	....	0.13	0.11	....	....	....	0.89	....	0.25	....	1.51	6.04
Broomsedge	1	0.33	....	0.16	0.03	....	....	....	1.97	....	0.13	....	0.71	5.14
Rice cutgrass	2	0.42	....	0.15	0.10	....	....	....	3.81	....	0.19	....	1.18	10.00
Average vegetative tissue		1.45	0.29	1.34	0.35	0.071	0.025	0.026	1.06	0.32	0.20	0.93	1.67	7.69
Average reproductive tissue†		1.76	0.20	0.18	0.19	0.030	0.011	0.009	0.24	0.19	0.29	0.35	2.65	3.64
Grand average		1.61	0.25	0.76	0.27	0.051	0.018	0.018	0.65	0.26	0.25	0.64	2.16	5.67
Per cent of K		100.00	15.53	47.20	16.77	3.168	1.118	1.118	40.37	16.15	15.53	39.75	134.16	352.17
Milliequivalents		41.18	10.87	37.92	22.20	5.673	0.655	0.645	92.66	16.22	24.21	18.05	462.53	....
Me. % of N		8.90	2.35	8.20	4.80	1.227	0.142	0.139	20.03	3.51	5.23	3.90	100.00	....

* The discharge potential or decomposition voltage of aqueous solutions of acids on platinum electrodes.

† Includes seed, fruit, and stems.

‡ Analyses reported by Snider (55).

nutritional habitat in which the species originated. The phylogenetic tolerance mechanisms in plants may be as definitely fixed as some of the other growth requirement characteristics. In certain humid forested regions the climatic and soil conditions are usually favorable for leaching of the stronger cations present in the soil. Plants native to such regions apparently have a tolerance mechanism which enables them to grow successfully where the relatively weak cations, such as the H ion, predominate in the soil colloids. Under such conditions it is customary to consider the so-called acid tolerance of certain crop plants. Climatic and soil conditions in a natural grassland area are usually favorable for accumulation of adequate or excessive quantities of certain mineral nutrients. Under such conditions many of the phylogenetic characteristics of plants native to such a habitat may be based largely upon tolerance mechanisms resulting from the excess concentration of minerals in the soil solution rather than upon specific nutrient requirements for growth processes. It may be expected, therefore, that certain mineral nutrient requirements become a major factor only when the crops are grown in a habitat significantly different from their native environment, such as may occur when grassland crops are transferred to forested areas. Where certain crops are subjected to excessive quantities of mineral nutrients, phylogenetic tolerance mechanisms, such as those of selective accumulation and selective exclusion, very probably protect the plants from excessive concentration of certain ions. The relatively large quantity of Si reported for tobacco is very probably partly due to fine sand adhering to the surface of the plant.

Selective accumulation of nutrients by plants

A number of investigators, including Robinson and Edgington (52), Hutchinson (30), Goldschmidt (26), Wallace *et al.* (59), Miller (40), and Cooper *et al.* (17 to 20), have reported on the selective accumulation of certain metals by some plants. Selective accumulation of Ca in plants, such as those of the legume, mallow, and nightshade families, through formation of organic compounds of relatively low solubility and low energy value, such as oxalates, acetates, malates, citrates, and pectates, illustrates one possible tolerance mechanism which protects the plant from excessive quantities of Ca ions in its tissue. Since such a characteristic is probably a more or less fixed phylogenetic tolerance mechanism which would be expected to operate over a wide range of concentration of different metals in the nutrient medium, the efficiency of the protective mechanism for inactivating certain ions may possibly result in a deficiency of some nutrients found in relatively low concentration in the nutrient medium.

Selective exclusion tolerance mechanisms of certain plants

In contrast to the protective mechanism by which excessively absorbed ions are largely inactivated through formation of relatively insoluble organic compounds in the plant, is the less well understood protective mechanism of selective exclusion of excessive ions not required for growth and reproduction. Most plants in the grass family, including such crops as wheat and other small grains indicated in table 5, do not absorb large quantities of Ca regardless of the concentration of ions in the nutrient media. Selective exclusion of Ca by certain tissues concerned with reproduction, such as seeds, fruits, tubers, and stems, may be related to the ontogenetic characteristics of the plants; whereas accumulation of Mg and P in seed and in other storage tissues concerned with reproduction indicates that there may be a very definite relation between Mg and P in reproduction and growth of plants. The quality of energy resulting from respiration and oxidation in germination and seedling growth may not be of the intensity required for efficient assimilation of P in so stable a form as $CaHPO_4$ (18).

Significance of accumulation of Mg and P and exclusion of Ca from seed

The accumulation of magnesium and phosphorus in seed, fruit, roots, tubers, and other reproductive tissues and the exclusion of Ca, Cl, and Si shown in table 5, indicate that there is a very definite relation between the Mg and P in reproduction and growth of seedling plants. This relationship suggests the necessity of an adequate supply of Mg for efficient utilization of P by seedling plants. Plants have apparently developed some mechanism for excluding excessive quantities of Ca from seed and other storage tissues concerned with reproduction. As most seeds germinate underground and are not exposed to sunlight, $(Mg)_3(PO_4)_2$ is probably the most stable phosphate compound that could be readily assimilated by the quality of energy available. The quality of energy resulting from respiration and oxidation processes would not be sufficient to assimilate P readily in so stable a form as $CaHPO_4$. The energy values involved in such reactions are included in tables 1 and 6. The required equivalent energy value of 4.20 volts for the decomposition voltage of $CaHPO_4$ can be calculated from oxidation-reduction potentials in tables 1 and 6 by adding +2.50 volts for the Ca ion and −1.70 volts for the discharge potential of H_3PO_4. This is equivalent to 2,939 A. of light energy, or the shorter ultraviolet wave in sunlight. The corresponding energy required for the decomposition of the $MgHPO_4$ is 3.25 volts, equivalent to 3,798 A., or the shorter wave length of sunlight. The quality of energy from respiration and oxidation processes of the stored organic constituents in seeds would probably be high enough for assimilation of $MgHPO_4$, but not for efficient assimilation of $CaHPO_4$. After seedling plants emerge from the ground, they are capable of absorbing the shorter wave lengths of sunlight, which represent a higher quality of energy than would be available in large quantities from respiration and oxidation processes. The older plants would be expected to assimilate $CaHPO_4$ more readily than plants in the seedling state.

It should be more clearly recognized that a higher intensity of energy is required for assimilation of P than for any other anion material, with the exception of F, shown in tables 1 and 9. It should also be recognized that the photosynthetic reactions in the syntheses of many organic compounds can occur at successive energy steps.

Some probable reactions occurring in selective accumulation mechanisms

The differential in the nutrient content of different plants grown in the same or similar nutrient media has definitely established the fact that some plants selectively accumulate certain nutrients while some selectively exclude certain nutrients. It is desirable to have a better understanding of some of the probable reactions taking place in some of the processes influencing accumulation and exclusion of particular nutrients. Since many of the photosynthetic reactions are concerned with the relative quantity of N and C available, it is of interest to consider some of the reactions affecting the relative supply of these two nutrients.

Many cultivated crop plants may be classified into two main groups according to their accumulated constituents. The Ca-accumulating group, including the legumes and members of the nightshade and mallow families, apparently also selectively accumulate Cl and exclude Si. The Si-accumulating group, including the grass, sedge, palms and some other oil-producing plants, apparently selectively exclude Ca. Data reported by Neller (42) on the mineral composition of grasses and legumes grown on sawgrass peat land in Florida are excellent examples of accumulation of Si by grasses and exclusion by legumes. The legumes are relatively high in Ca, Fe, P, protein, and ash. The carbonaceous grass crops are relatively high in Mg and Si and relatively low in Ca, Fe, P, and ash. Elgabaly and Wiklander (22, 23, 24) reported data on the effect of the acidoid content of plants on the uptake of Na and Ca. Roots of the Ca-accumulating pea plant contained larger quantities of Ca than did roots of Si-accumulating barley, which contained relatively large quantities of Na. Lundegardh (36, 37), in a comprehensive study of salt accumulation in wheat roots, has pointed out the competition between organic acids and inorganic anions, and the depressing effect of the organic anions upon the absorption of inorganic anions and a corresponding increase in the absorption of cations. Cooper *et al.* (20) have shown by ratios of elements in the plant that the grasses have a greater relative capacity to accumulate anions than the legumes. The capacity to assimilate CO_2 seems to be much greater in the grasses than in the legumes. Mattson *et al.* (39) have presented data showing the wide difference in the root acidoids of rye and yellow peas. The acidoid content is 29.5 me. per 100 gm. for the rye roots and 71 me. per 100 gm. in the pea roots. The pH of the base-unsaturated material is 3.90 and 3.38, respectively. The exchange capacity for the roots of the Leguminosae is more than twice as great as that for the Gramineae.

Many of the Ca-accumulating plants are usually relatively high in N and are classified as proteinaceous crops. These crops require a relatively large quantity of the alkali metals for normal development and for production of a satisfactory yield of carbonaceous materials. It is, therefore, interesting to note some of the solubility values included in table 3, which may significantly affect the relative quantity of CO_2 available for synthesis of complex organic compounds.

These solubility values suggest that the Ca accumulated by plants would be largely adsorbed as nitrates or chloride. The large amount of Ca absorbed by certain plants in the form of $Ca(NO_3)_2$ suggests the desirability of considering some of the possible types of reactions occurring in some of the Ca-accumulating plants for comparison with possible reactions in Si-accumulating plants.

Possible type of Ca-tolerance mechanism reactions in Ca-accumulating plants

Since $Ca(NO_3)_2$ and $CaCl_2$ are the only highly soluble Ca salts generally found in soils, much of the Ca accumulating in plants is probably derived from these two compounds. Absorption of $Ca(NO_3)_2$ from the soil and of CO_2 from the air may result in the following type of reactions and combinations in the plant: $Ca(NO_3)_2 + H_2CO_3 \rightleftharpoons CaCO_3$ and/or CaC_2O_4, Ca-malate, Ca-citrate + 2 $HNO_3 \rightarrow$ amino acids → proteins → proteinaceous vegetation. Such reactions may occur in the legume, mallow, and nightshade families.

The potential phylogenetic capacity of the plant to synthesize organic acids in different nutrient media may largely determine the quantity of Ca absorbed and accumulated in the form of low-solubility organic compounds. Existence of organic anions in the plant may tend to buffer absorption of other anions and may significantly decrease the intensity of absorption of CO_3 ions and significantly affect the total production of dry matter. Formation of relatively low solubility organic compounds would provide a possible mechanism for depletion of the Ca-ion concentration and for continuous absorption and accumulation of Ca in the plant, probably in proportion to the phylogenetic capacity of the plants grown in various nutrient media to synthesize acid materials. Such a system of reactions would favor the synthesis of organic compounds relatively high in minerals and proteins and a relatively low production of total dry matter.

Possible type of reactions occurring in Si-accumulating plants

Since K_2SiO_3 and Na_2SiO_3 are the only highly soluble silicate compounds in soils, much of the Si accumulating in plants is probably derived from one or the other of these silicates. Absorption of K_2SiO_3 from the soil and of CO_2 from the air may result in the following type of reaction in the plant: $K_2SiO_3 + H_2CO_3 \rightleftharpoons (H_2SiO_3 \rightarrow H_2O + SiO_2) + (K_2CO_2 \rightarrow$ carbon compounds → carbonaceous vegetation). Such reactions may occur in certain highly carbonaceous crops in the grass, sedge, and palm families. Plants in this group would very probably have a relatively low phylogenetic capacity to synthesize organic acids. Formation of H_2SiO_3 which would very probably break down into H_2O and SiO_2, would provide a possible mechanism for depletion of the SiO_3 ion concentration and for continuous absorption and accumulation of Si in the plant. Depletion of the SiO_3-anion concentration in the plant would very probably provide for a high intensity in the absorption of CO_2 and result in synthesis of highly carbonaceous compounds. The relatively low organic acid content of such plants would result in synthesis of organic compounds relatively low in minerals and proteins, but with a relatively high production of total dry matter. Ca-accumulating plants generally are classified among the most nutritious food plants. It should be recognized, however, that a very large proportion of the food products for the entire animal kingdom is derived directly or indirectly from Si-accumulating plants with a relatively low total mineral content, which is characteristic of many of the crops in the grass family. Such possible reactions would suggest that one of the important functions of alkali metals in plant nutrition may be related to the capacity of these metals to maintain a soluble supply of carbonates for photosynthetic reactions. The foregoing simple chemical reactions may illustrate some of the initial reactions in the nutritional processes of some crop plants. The relative magnitude of the successive energy levels involved in such reactions may be one of the factors in determining the relative synthetic efficiency of different plants. Plants requiring the minimum quanta reaction in the synthetic reactions may be expected to have the most efficient photosynthetic mechanisms, which should be a significant survival characteristic.

It is interesting to compare the maximum production of some of the highest producing crop plants in the Ca- and Si-accumulating groups, such as Ca-accumulating sugar beets and Si-accumulating sugar cane and likewise alfalfa and corn, soybeans and sorghum, cotton and pearl millet, and clovers and grasses.

Olsen (45) has reported that in some plant species the quantity of oxalic acid produced and the amount of Ca absorbed are related. Some of his cultures showed a negative relation between dry-matter production and concentration of Ca in the nutrient media, and a positive correlation between K concentration and production of dry matter. The existence of selective accumulating mechanisms suggests one of the important factors in determining the relatively constant content of different nutrients in plants over a wide range of concentration of ions in the nutrient medium. Critically low concentrations of certain nutrient ions are often necessary in the medium to influence significantly the mineral composition of plants. It has been noted by Mattson *et al.* (38) that the chemical composition of plants is often apparently more definitely related to certain phylogenetic characteristics, such as Ca-precipitants, than to concentration of materials in the nutrient medium.

Olsen (46), in water culture experiments with *Sinapis alba, Dianthus barbatus, Hordeum distichum,* and *Tussilago farfarus,* found that with a low content of K it was possible to demonstrate a decrease in production of dry material by Sinapis, Dianthus, and Hordeum when the concentration of Ca in the nutrient solution exceeded a certain value; but when K was present in liberal amounts in the nutrient solution no instance was recorded of any harmful effects of Ca ions on the production of dry material in the four species. With increasing Ca concentration of the nutrient solution, the first three species absorbed increasing amounts of Ca but decreasing amounts of Mg and P. The behavior of Ca-accumulating *Tussilago farfarus* was found to be contrary to that of the other three species. The K content of this plant increased with the rising Ca concentration of the nutrient solution. The relatively high total milliequivalent content of Ca, Mg, and K reported suggests that the Ca may have been accumulating in the plant in the form of low solubility organic Ca compounds, which would not be expected to depress significantly the uptake of K.

GROWTH OF PROTEINACEOUS AND CARBONACEOUS CROP PLANTS DIFFERING IN NUTRITIVE VALUE

Light energy has been one of the most significant factors in building the organic world. The quality of light, or the quanta of energy utilized, largely determines the nature and configuration of the substances produced as well as the quantity synthesized.

Various types of plants differ in their light-absorbing properties, and the quality of the radiant energy absorbed largely determines the degree of instability of the absorbing substance. When exposed to light energy, optically active substances differ in their instability. Certain substances differ in their ability to absorb *d*- and *l*-circularly polarized light. In organic chemical synthesis the substance formed is generally symmetrical in the configuration of atomic groups of molecules, or equal quantities of the two *d*- and *l*-optical isomers are formed (27). When environmental conditions of synthesis are symmetrical in properties, the products are symmetrical in arrangement. The tissues of living things are asymmetrical and in their action upon food materials select those whose sterio-configurations best fit their own.

Since the presence of asymmetrical compounds influences the symmetry of synthetic products, it is interesting to note that most of the sugars belong to the *d*-family of isomers and most of the proteins to the *l*-isomers. Under certain conditions the reverse of these configurations may be formed, depending upon the nature of their formation.

Attention has been directed to the relatively small amounts of Ca in the carbonaceous parts of plants such as seeds, fruits, roots, and tubers and also to the amount of Mg, which is often greater than the quantity of Ca, in seeds, roots, and tubers. Production of carbonaceous crops generally is associated with a relatively large supply of available K. Since production of carbonaceous material is the result of assimilation of CO_2, the solubility of the bicarbonate and of the carbonates of K, Na, and NH_4 as compared with the solubility of $CaCO_3$ is of interest. A large quantity of $Ca(HCO_3)_2$ probably would not exist in plants, as the conditions would be favorable for formation of $CaCO_3$ or other relatively insoluble Ca compounds. These relations would indicate that the presence of relatively large quantities of Ca in the plant would be unfavorable for maintenance of an ample supply of CO_2 for assimilation. In the presence of large quantities of Ca, the NO_3^- and the Cl^- are the only common nutrient anions that would be readily soluble. Therefore, synthesis of proteins may be greater than that of carbohydrates where the supply of CO_2 is limited. The relative quantities of CO_2 and N available to plants may determine the differential in the synthesis of carbonaceous and proteinaceous materials, depending upon the relative quantities of the anions of these nutrients available for photosynthetic reaction.

RELATION OF EXOTHERMIC AND ENDOTHERMIC REACTIONS TO NUTRITION OF ORGANISMS

The discharge potential reactions occurring in such photosynthetic reactions as the evolution of O_2, suggest the desirability of considering the energy of formation, decomposition voltage, and discharge potential of some common nutrient compounds. The approximate exothermic energy given off in the formation of some diatomic and simple compounds is shown in table 6. The standard electrode potentials represent the energy of ion formation and of hydration.

The energy of hydration of some of the smaller ions may be relatively high, which results in a relatively high oxidation-reduction voltage value. The energy of formation is expressed in volt-Faradays, Ångstroms, and color of light. These values can be converted from one to another very easily by use of Einstein's photochemical equation. This equation and the factors used in conversion of one mode of expression of energy into another (25, 31, 51) are as follows:

$$E = Nh_v = Nh_{\lambda}^{c} \text{ ergs per mole}$$

$$\text{Ångstroms} = \frac{12{,}345}{\text{volt-Faradays}}$$

$$\text{Volt-Faradays} = \frac{12{,}345}{\text{Ångstroms}}$$

$$\text{Volt-Faradays} = \frac{\text{gram calories}}{23{,}058}$$

$$\text{Gram calories} = \text{Volt-Faradys} \times 23{,}058$$

where E = energy, N = Avogadro number, h = Planck constant, v = frequency of radiation, c = velocity of light, and λ = wavelength in cm.

Conversion of the energy values involved in various reactions to equivalent volt-Faradays, Ångstroms, and color of light shows more clearly the relationship between these values (15). Data on the approximate energy of formation of metallic chlorides are included in table 6. These values are the sum of the standard electrode potentials of ions. A value of −1.36 volts was used for the electrode potential of Cl. The standard electrode potentials of the metals used can be determined by subtracting this Cl value from the total free energy decrease in the formation of the compounds. Since there is a general tendency for each element to form compounds resulting in the maximum amount of free energy decrease, the stronger ions would be expected to form more energy-stable compounds. The values for energy of formation (table 6) suggest the compounds that would likely predominate in a solution containing various ions. It is interesting to note the great difference in the decomposition voltages H_3PO_4 and $CaHPO_4$ and $Ca(OH)_2$, $CaCl_2$, and CaF_2. These relatively high energy values would definitely suggest that P and F could be more readily assimilated by both plants and animals in less stable form than either $(Ca)_3(PO_4)_2$ or CaF_2. If light energy equivalent to the decomposition potential of the compound is assumed to be desirable in the synthesis of compounds from nutrients, it is easy to understand why the less energy-stable compounds may be more readily assimilated by plants and animals.

QUALITY OF ENERGY AVAILABLE IN SUNLIGHT

Since light energy is required in assimilation of plant nutrients or in synthesis of organic compounds, it is desirable to consider the quality of the light available for plant growth. The available energy for photosynthesis on the surface of the earth is almost entirely traceable to sunlight. The ranges in the energy values in the solar spectrum as it reaches the earth are included in table 7. The wave lengths range from around 2,900 A. in the ultraviolet to 30,000 A. in infrared light. The corresponding energy values range from 98,227 to 9,454 gram calories and from 4.26 to 0.41 volt-Faradays. The position of maximum energy, or greatest intensity, occurs within the visible spectrum. The quality of light is often much more important than the intensity in producing photochemical reactions in plants in the synthesis of certain organic compounds. Energy exists in larger units in the shorter wave lengths of light. The energy value of the Einstein for ultraviolet radiation is approximately two to two and one-half times that for red light. The energy values reported in table 7 show qualitatively why certain photochemical reactions are more frequently initiated by ultraviolet than by visible light. Photochemical reactions may be accompanied by a free energy increase. One of the most important endothermic reactions in the plant kingdom is the conversion of water and carbon dioxide by sunlight into complex organic molecules.

TABLE 6

Approximate relative heat of formation or decomposition voltage and discharge potential of some nutrient electrolytes and the corresponding equivalent energy value in color of light

ELECTROLYTE	HEAT OF FORMATION IN VOLT-FARADAYS	EQUIVALENT LIGHT ENERGY	
		Ångstroms	Color
$CuCl_2$	1.02	12,103	Infrared
HCl	1.36	9,077	Infrared
$FeCl_3$	1.40	8,818	Infrared
$NiCl_2$	1.58	7,813	Infrared
$CoCl_2$	1.65	7,482	Red
$FeCl_2$	1.80	6,858	Red
NH_4Cl	1.91	6,463	Orange
$ZnCl_2$	2.12	5,823	Yellow
$MnCl_2$	2.46	5,018	Green
$AlCl_3$	2.66	4,641	Blue
$MgCl_2$	2.91	4,316	Violet
$CaCl_2$	3.86	3,198	Ultraviolet
NaCl	4.07	3,033	Ultraviolet
KCl	4.28	2,884	Ultraviolet
H_3PO_4	1.70*	7,262	Red
$Ca(OH)_2$	2.91	4,242	Violet
$CaCl_2$	3.86	3,198	Ultraviolet
$Ca_2H_2(PO_4)_2$	4.20*	2,939	Ultraviolet
CaF_2	4.46	2,768	Ultraviolet

* Value for anion represents decomposition voltage or discharge potential of aqueous solutions of acids on platinum electrodes.

The approximate energy of formation of simple electrolytes is equal to the sum of the standard electrode potentials. At sea level the short-wave limit of the solar spectrum is around 2,900 A. or 4.26 equivalent volts to 30,000 A. or 0.41 equivalent volt. These energy values may be expressed in volts, wavelength of radiant energy, or color of light.

QUALITY OF RADIANT ENERGY ABSORBED BY CHLOROPHYLL

Photosynthesis is generally recognized as one of the most important endothermic reactions; therefore, special consideration should be given to light energy absorbed by chlorophyll (10, 15). It may be logical to assume that during the molten stage in the evolution of the earth there was no chlorophyll. Since chlorophyll is apparently a product of photosynthesis, it is desirable to consider some of the primary light-energy-absorbing materials that may have contributed to the genesis of primordial chlorophyll. The data in table 8 record the range in the light-absorption bands in chlorophyll expressed as Ångstroms and as equivalent volts. The hypothesis that life may have originated in the hydrosphere suggests consideration not only of the exothermic reactions in the formation of metallic nutrient chlorides, since a preponderance of the Cl is found in the hydrosphere, but also of the absorption bands in chlorophyll, which are very probably di-

TABLE 7

Approximate equivalent energy value of the Einstein at different wave lengths of the solar spectrum expressed in color of radiation, wave length in Ångstroms, gram calories, and volt-Faradays

COLOR OF RADIATION	ENERGY VALUES		
	Wave length in Ångstroms	Gram Calories	Volt-Faradays
Infrared	30,000–7,500	9,454–38,046	0.41–1.65
Red	7,500–6,500	38,046–43,810	1.65–1.90
Orange	6,500–5,900	43,810–48,191	1.90–2.09
Yellow	5,900–5,750	48,191–49,575	2.09–2.15
Green	5,750–4,900	49,575–58,106	2.15–2.52
Blue	4,900–4,550	58,106–62,487	2.52–2.71
Violet	4,550–3,950	62,487–72,172	2.71–3.13
Ultraviolet	3,950–2,900	72,172–98,227	3.13–4.26

TABLE 8

Close agreement of endothermic reaction values in absorption bands in chlorophyll with exothermic reactions or equivalent energy of formation or decomposition voltage of certain nutrient electrolytes, particularly the chlorides

BAND	RANGE OF ENERGY IN ABSORPTION BANDS		ENERGY OF FORMATION OR DECOMPOSITION VOLTAGE OF ELECTROLYTE	
	Ångstroms	Equivalent Volts	Material	Equivalent Volts
I	6800–6371	1.81–1.94	$FeCl_2$	1.80
II	6250–6000	1.98–2.06	$CrCl_2$	1.92
III	5860–5640	2.11–2.19	$ZnCl_2$	2.12
IV	5390–5230	2.29–2.36	....	....
V	5040–4890	2.45–2.52	$MnCl_2$	2.46
VI	4710–	2.62–	$AlCl_3$	2.66
....	4400–4300	2.80–2.87	$MgCl_2$	2.91
Vitamin A concentrate		3.85*	$CaCl_2$	3.86
Prevention of rickets		4.08–4.26	$CaHPO_4$	4.20

* Vitamin A concentrate, biosterin, is characterized by marked selective absorption at 3,200 A. or 3.85 equivalent volts. It has been suggested that vitamin A plays a role through its oxidation-reduction action.

rectly related to the endothermic reactions in the synthesis of organic compounds. The very close correlation between the quality of energy absorbed by chlorophyll and the free-energy decrease in the formation of mineral chlorides, or the decomposition voltage, definitely suggests that certain metallic compounds may have been among the primary light-energy-absorbing compounds in the genesis of primordial chlorophyll. Seemingly, the correlation between the quality of radiant energy absorbed by chlorophyll and the decomposition voltage of mineral salts is too close for coincidence. A close analysis of these relationships may conceivably provide the key for interpretation of many of the complex reactions in photosynthesis. The absorption bands in chlorophyll definitely suggest that some minor metallic nutrient may have been involved in some of the chemosynthetic reactions which may have preceded the primordial chlorophyll. The radiant energy absorbed by chlorophyll is approximately the same as the decomposition voltage of certain nutrient salts; therefore, it seems logical to assume that absorption of radiant energy by plants may result in reducing certain nutrient compounds to the elemental state. Such reduction in plants may provide a mechanism for transfer of energy at characteristic energy levels in the synthesis of organic compounds, affording an opportunity for different nutrient elements to form different compounds.

It is also interesting to note that vitamin A concentrate, biosterin, is characterized by marked selective absorption of radiant energy at 3,200 Å or 3.85 equivalent volts, which is very close to the energy of formation or decomposition voltage of $CaCl_2$. The quality of ultraviolet radiation effective in preventing rickets is in close agreement with the decomposition voltage or the discharge potential of $CaHPO_4$. Laurens (34), in his comprehensive report on the physiological effect of radiant energy, has shown that the wave length of 2,968 A., equivalent to 4.16 volts, is most potent in the cure of rickets in rats, 3,020 A., equivalent to 4.09 volts, being perhaps one fourth as effective.

ENERGY REQUIRED IN REDUCTION AND ASSIMILATION OF SOME ANIONS AND EVOLUTION OF O_2

Some of the possible steps in the energy of formation of nonmetallic complex anions are very probably definitely related to the quality of radiant energy utilized in chemosynthesis and photosynthesis. The anions in table 9 are arranged in order of energy required for initial reduction. The equivalent energy required for reduction and the release of O ranges from infrared to ultraviolet radiation, or from 0.85 to 3.79 volts and from 14,523 to 3,257 A.

The energy required to release O from the various complex anions differs widely. The energy reactions involved in reduction of the O in complex anions and evolution of elemental O is one of the major processes in photosynthesis. It has been observed that some bacteria can reduce certain materials to the elemental state (27, 58). Formation of elemental S, N, H, and O in plants illustrates some of the typical reduction reactions very probably occurring in chemosynthesis and photosynthesis.

Leeper (35) has criticized the concept that there is a correlation between the relative strength of ions as indicated by the standard oxidation-reduction potentials and the initial intensity of absorption and utilization of nutrients by many plants. A systematic arrangement and a critical consideration of available information on the chemical composition of a wide variety of plants grown over a wide range in soil and climatic conditions should be sufficient to suggest to anyone the relation between the relative strength of nutrient ions and the content of some nutrients in plants. Leeper suggests that the relationship holds for K, Mg, and Fe, but does not hold for Na. Since different plants vary widely in Na content, probably depending upon a differential in the effectiveness of their characteristic phylogenetic Na-tolerance mechanisms, it is necessary to designate the plant under consideration before concluding that Na is an exception. His statement indicates a lack of understanding of the content and function of Na in the nutrition of many plants.

TABLE 9

*Approximate equivalent energy required for reduction of anions, expressed as color of light radiation, wave length of radiation in Ångstroms and volts**

OXIDIZED ION	EQUIVALENT REDUCTION ENERGY			REDUCED ION
	Color radiation	Ångstroms	Volts	
$HSeO_4^-$	Infrared	14,523	0.85	$HSeO_3^-$
NO_3^-	Infrared	11,757	1.05	NO_2^-
TeO_4^{--}	Infrared	8,398	1.47	TeO_3^-
BO_3^{--}	Red	6,935	1.78	BO_2^-
$H_2AsO_4^-$	Orange	6,235	1.98	$H_2AsO_3^-$
HSO_4^-	Blue	4,572	2.70	HSO_3^-
HCO_3^-	Violet	4,332	2.85	HCO_2^-
$H_2PO_4^-$	Ultraviolet	3,685	3.35	$H_2PO_3^-$
$H_2PO_3^-$	Ultraviolet	3,257	3.79	$H_2PO_2^-$

* Oxidized ion + equivalent reduction energy = reduced ion $+\frac{1}{2}O_2$.

Leeper's interpretation of the relationships under consideration is revealed in the following quoted statement: "Theoretically this rule does not make sense, since these elements are not in the metallic state at any time." It is surprising that one posing as a competent critic seemingly has not taken into consideration the general application of the Law of the Photochemical Equivalent resulting in the appearance of elemental materials such as S, N, H, and O in the plant from chemosynthetic and photosynthetic processes (27, 58).

Because many nutrients are solids in the elemental state and cannot be evolved like those that are gases is not sufficient evidence of any significant difference in the initial energy reaction involved in assimilation of the different nutrients. O_2 is classified as one of the most strongly electronegative elements. A relatively high quality of energy is required to force the valence electrons from the ionic state to form elemental O. There is very little theoretical reason to doubt that other less electronegative nutrient elements would undergo similar thermodynamic reactions to that of O, which has a relatively stable molecular structure and is capable of being readily evolved as a gas in photosynthesis. Since all the statements on the subject under consideration can be verified from existing information, further attention to a criticism that offers no constructive suggestions on the relationships involved does not seem worthwhile.

It is interesting to note that, in large quantities, all of the anion compounds above the SO_4 ion in the grouping in table 9 are toxic to animals. In some instances the toxicity may be related to the unsaturated reduced anion, which may react like the unsaturated reduced CO_3 ion in forming stable compounds with constituents of blood or other tissues. Any anion that can be readily reduced by the animal system may be toxic, particularly when consumed in relatively large quantities (53). The intensity of the energy necessary for reduction of HSO_4^-, CO_3^-, and HPO_4^- is too high to allow ready reduction by the animal system. PO_4^- H_2 is the most energy-stable anion in the group. This stability makes PO_4^- H_2 one of the most difficult anions to assimilate. In most nutritional complexes it is desirable to have P in less energy-stable compounds than $CaHPO_4$ to ensure efficient synthesis of this element by many types of organisms. The relatively large quantity of energy required for reduction of PO_4 ions suggests the significance of P in the synthesis of organic compounds capable of supplying relatively large quanta of energy in digestion and respiration processes. Some common bond-energy values that might influence such relationships have been summarized by Remick (50).

The less energy-stable compounds would very probably be the most satisfactory source of energy for some of the chemosynthetic processes in obligate autotrophic bacteria in soils. The chemosynthetic reactions in facultatively autotrophic organisms very probably take place at a higher energy level than is characteristic of intensity of energy utilized by the autotrophic organisms. Harvey (27) has suggested that the facultatively autotrophic organisms may be the connecting link between the autotrophic and the more abundant heterotrophic bacteria.

The relatively low intensity of energy, equivalent to infrared light, required in initial reduction of nitrates suggests that N assimilation may occur at relatively low energy levels as compared with the CO_3 ion, which requires energy of quality equivalent to violet light. Burstrom (5, 6) reported on the energy values involved in NO_3 assimilation. The relative quality of energy utilized in chemosynthesis and photosynthesis may be a very significant factor in determining survival or predominance of certain types of organisms. The relative significance of the quality of energy involved in such a reaction is illustrated by the very high NO_3 content of many common vegetables found on the markets, as reported by Wilson (61). The danger of accumulation of toxic quantities of nitrates in food plants may have a very significant effect upon the general health and nutrition of farm animals and man. Many commercial growers believe that heavy applications of NO_3-N are effective in reducing insect injury to some vegetable crops. In certain cases the decrease in injury may be related to the accumulation of sufficient soluble unassimilated metallic nitrates in the plant sap to be toxic to some insects.

As suggested by Harvey (27), the assumption of a photosynthetic function by plants has led to major developments in the organic world. The predominance of C synthesis in higher plants seems to have resulted in a loss of ability to fix atmospheric N. Since the acquisition of N compounds is one of the major factors limiting plant growth, failure to retain the N-fixing capacity may be considered a distinct loss to the higher plants. It seems that retention of this ability must have been incompatible with the performance of some other important function, such as photosynthesis or the increased efficiency in C assimilation at a higher energy level than is necessary for assimilation of N. It has been noted that certain bacteria which produce H under anarobic conditions also fix atmospheric N. If the fixation of atmospheric N, which is at a relatively low energy level, is dependent upon essentially anaerobic conditions in the cell, it may be perceived that higher plants must have necessarily lost this ability when they began photosynthesis and the liberation of O_2. It should be noted that if the higher plants, with their efficient assimilation of CO_2, had retained or acquired the capacity to utilize atmospheric N, the almost unlimited supply of this N, which constitutes about 78 per cent of the atmosphere as compared with the 0.03 per cent of CO_2, would have soon tied up all the CO_2 available for plant growth.

TABLE 10

*Some common equivalent oxidation-reduction reactions occurring in certain physiological processes that take place on approximately the same energy level**

REACTION AND EQUIVALENT ENERGY (VOLT-FARADAYS) INVOLVED	EQUIVALENT LIGHT ENERGY	
	Ångstroms	Color
$NO_3^- = NO_2^- + 0 + 1.05$	11,757	Infrared
$H_2O + O = H_2O_2 + 1.03$	11,985	Infrared
$CuCl_2 = Cu + 2Cl + 1.02$	12,103	Infrared
$Mn^{++} = Mn^{+++} + 1.07$	11,537	Infrared
$BO_3^{---} = BO_2^- + 0 + 1.77$	6,974	Red
$FeCl_2 = Fe + 2Cl + 1.80$	6,858	Red
$H_2AsO_4^- = H_2AsO_3^- + 0 + 1.98$	6,235	Orange
$CrCl_2 = Cr + 2Cl + 1.92$	6,430	Orange
$H_2CO_3^- = H_2CO_2^- + 0 + 2.85$	4,332	Violet
$MgCl_2 = Mg + 2Cl + 2.91$	4,316	Violet
$H_2PO_4^- = H_2PO_3^- + 0 + 3.35$	3,685	Ultraviolet
$CaC_2O_4 = Ca + C_2O_4 + 3.35$	3,685	Ultraviolet
$H_2PO_3^- = H_2PO_2^- + 0 + 3.79$	3,257	Ultraviolet
$CaCl_2 = Ca + 2Cl + 3.86$	3,198	Ultraviolet
$CaHPO_4$ decomposition potential.......4.20	2,939	Ultraviolet
Effective rays in preventing rickets.....4.16	2,968	Ultraviolet

* These values were obtained from International Critical Tables 5: 169–207. 1929.

Approximate equivalent energy in solar spectrum ranges from 0.41 to 4.20 volt-Faradays, which is equivalent to 30,000 to 2,900 A.

Values in tables 1, 9, and 10 show that the energy of formation of $MgCl_2$ and the energy required for reduction of CO_3^{--} are practically identical. This is an interesting relation, as Mg is a constituent of chlorophyll and apparently functions in the synthesis of C compounds. It has been generally assumed that the initial energy reaction in the synthesis of C is the reduction of the HCO_3^- and the liberation of O_2. Van Niel (57, 58) has directed attention to oxygen isotope studies which show that O_2 evolved in certain photochemical reactions comes from H_2O and not from HCO_3^-. The energy values in table 1 show a theoretical decomposition voltage of 1.23 for H_2O, which is much less than the 2.85 volts required for reduction of HCO_3^-. These energy values would definitely support Van Niel's suggestion that photosynthesis of green plants represents an oxidation-reduction process induced by light and proceeding with the participation of special pigments in which CO_2 is the ultimate H acceptor and H_2O the H donor, resulting in evolution of the O_2 from the H_2O.

Some exothermic and endothermic reactions characteristics of certain nutrient compounds

The relation between the exothermic reaction in the formation of metallic nutrient compounds and the endothermic reaction in the reduction of certain anions is included in table 10. The approximate free energy decrease in the formation of certain metallic compounds and the free energy increase in the reduction of some anions may be definitely related to the essentiality of certain nutrients for some plants, as suggested by Steinberger (56). It is interesting to note the relatively low energy level at which NO_3^- is reduced. Some of the energy reactions occurring at comparable levels are the formation of H_2O_2, the change of Mn^{--} to Mn^{---}, and the free energy increase in the formation of $CuCl_2$. The fact that Cu and Mn deficiencies in plants are most likely to occur on soils relatively high in nitrates may be partly due to the solubility of the nitrates of these metals, which may result in their loss from the soil in drainage water. The close agreement between endothermic energy required for reduction of these anions and the exothermic energy of formation of metallic salts suggests that several energy reactions may be occurring at levels comparable to the endothermic energy absorbed by chlorophyll in the synthesis of organic compounds. Burstrom (6) has pointed out the relation between Mn and assimilation of NO_3.

In the forward movement in the scale of plant evolution, the complexity of the organic systems gradually increases. Production of lignin, which is apparently synthesized at a relatively high energy level, allowed expansion of land plants to great size, enabling them to spread into the air large surfaces capable of photosynthesis. Production of bone primarily from Ca, P, and F at a higher energy level than lignin represents an advancement in the animal kingdom comparable to production of lignin by plants. The thermodynamic characteristic of the constituents of bones suggests that bone material is synthesized at an energy level near the upper limit of solar radiation; in other words, animals have utilized for bone structure the most energy-stable compounds that could be readily synthesized by the energy available in sunlight. An unfavorable combination of the more energy-stable compounds utilized may lead to disturbances in the synthesis of bone, resulting in rickets and other unsatisfactory conditions, unless the optimum quality of radiant energy or the equivalent quality of energy from the digestion and oxidation of organic compounds is available.

Since many of the synthetic reactions can occur either from absorption of a single quantum of energy or from absorption of the equivalent quality of energy in two or more quanta reactions, the rate or efficiency of synthesis may not meet the optimum growth requirements of the organisms. These relationships indicate that evolutionary advancement in organisms is more definitely related to efficiency of synthetic reactions than to mere capacity of synthesizing any particular products.

In our consideration of many important biological reactions, probably too much emphasis has been placed on ability to produce certain reactions rather than on efficiency in the production of material. Plants with the most efficient photosynthetic mechanisms and animals with the most efficient bone-synthesis mechanisms are likely to be among the dominant organisms.

TABLE 11

Cathodic and anodic overvoltage values for hydrogen and oxygen with different metal electrodes and approximate decomposition voltages of aqueous solutions with the evolution of hydrogen and oxygen

ELECTRODE	OVERVOLTAGE IN VOLTS			SUMMATION PLUS 1.2 VOLTS FOR WATER*
	Hydrogen cathode	Oxygen anode	Summation	
Platinized platinum	0.00	0.25	0.25	1.45
Iron	0.08	0.25	0.33	1.53
Smooth platinum	0.09	0.45	0.54	1.74
Nickel	0.21	0.06	0.27	1.47
Copper	0.23	0.05	0.28	1.48
Cadmium	0.48	0.43	0.91	2.11
Lead	0.64	0.31	0.95	2.15
Zinc	0.70	....	....	....
Mercury	0.78	....	....	....

* The discharge potential for water of 1.2 volts is the theoretical reversible electromotive force of the hydrogen-oxygen cell. The approximate decomposition voltage for any combination of electrodes of any aqueous solution resulting in the evolution of hydrogen and oxygen is equivalent to the summation of the overvoltage of hydrogen and oxygen on the different electrodes plus 1.2 volts, which is the theoretical reversible decomposition voltage of H_2O.

Overvoltage effects in nutrition

The cathodic and anodic overvoltages reported by Glasstone (25) for H and O on different electrodes (table 11) may be of significance in interpreting some of the endothermic reactions in photosynthesis. The overvoltages vary with the nature of the electrode surface, as shown by smooth and platinized Pt. The approximate decomposition voltage for any combination of electrodes of aqueous solutions resulting in evolution of H_2 and O_2 is equivalent to the summation of the overvoltage values for H and O on the different electrodes plus 1.2 volts, which is the theoretical reversible decomposition voltage of H_2O. These values suggest that there may be a differential in the relative discharge potential of the H ions in combination with different metals. Certain metals may increase the discharge potential of the H ions and enable these ions to enter into organic combinations at a higher bond-energy value than the theoretical discharge potential of 1.2 volts for the simultaneous liberation of H_2 and O_2 from water.

The overvoltage values for O would also very probably result in entry of the O into organic combinations at relatively higher bond-energy values rather than when discharged as a gas at the theoretical decomposition value for H_2O. Data in table 9 show considerable variation in intensity of the binding of O in different oxidized anions, ranging from 0.85 volts for the SeO_4 to 3.79 volts for the PO_3 ion.

Some of the significant functions of certain of the minor mineral nutrients may be definitely related to relative energy levels in different combinations at which the H and O ions are discharged, resulting in the evolution of H_2 and O_2.

Possible function of certain minor nutrients

Since many of the energy reactions in photosynthetic processes result in the discharge and evolution of O_2, it is helpful to consider some decomposition voltages and discharge potential values in common use by electrochemists. The electrochemist utilizes the overvoltage value for H on different metal electrodes included in table 11 in electroplating and other processes where it is desirable to increase the discharge potential of H ions. The overvoltage values for O also show that there is a differential in the strength of the O ions with different metal electrodes.

These H and O overvoltage values on different electrodes may be very significant in determining some of the specific functions of such minor nutrients as Mg, Zn, Fe, Co, and Cu, which have a differential electrode effect upon the relative strength of H^+ and O^{--}. These materials may increase the relative strength of H and O ions, which would permit these elements to enter organic compounds at a higher energy-bond strength than would be possible if the O were discharged as a gas at the theoretic discharge potential of H_2O, as shown in tables 1, 9, and 11.

All the energy values discussed in this paper definitely suggest that those interested in investigating the fundamental phases of soil fertility and plant and animal nutrition will have to become more familiar with thermodynamics, electromotive force, electrochemistry, photochemistry, and spectroscopy. Use of available information in the physical sciences could lead to very rapid progress in biology in the near future. If, for example, there is a differential in the strength of the H and O ions in combination with the different minor plant nutrients, as might be inferred from certain electrochemical reactions, these differences may be useful in investigating the energy values of the bonds between these and other atoms in photochemical processes occurring in the synthesis of organic compounds possessing different energy and nutritive values.

Some possible light energy factors influencing the nutritive value of foods

The energy reaction in photosynthetic processes resulting in reduction and evolution of O suggests the desirability of considering the relation of energy evolved in the decomposition voltage and discharge potential of other nutrient compounds. If such a strong electronegative element as O is discharged and evolved as a gas in photosynthesis, there are reasons for expecting similar energy reactions to occur in solid anions, which cannot be evolved as a gas in photosynthetic reactions. The energy required for reduction of different anions and evolution of O (table 9) shows that there is a differential in the intensity of the energy binding the O in the different anions. These thermodynamic values would definitely suggest that comparable oxygen-energy bonds would be expected in organic compounds. If the nutritionist is to determine the specific function of many of the food constituents, such as the various vitamins, he will very probably have to consider the specific quality of the bond energies or the intensity of the various oxidation-reduction reactions in nutritional processes.

Since some of the exothermic energy reactions occurring in the formation of certain nutrient compounds from elements are in very close agreement with the light-absorption bands in chlorophyll, or the endothermic reactions occurring in photosynthetic processes, it is desirable to consider the possible effects of the relative strength of ions utilized by plants on the quality of light required in photosynthesis and the nutritive value of the different organic compounds synthesized from absorption of the different qualities of light energy. Very probably, plants requiring a relatively large quantity of the stronger nutrient ions for optimum growth will be intolerant of shade and will require light of relatively high quality comparable with the strength of ions required for growth. Conversely, plants making optimum growth with a relatively small quantity of strong ions and more of the weaker ions would be expected to be tolerant of shade and to make optimum growth with relatively low quality and intensity of light. It would be expected that the relative bond-energies in some of the organic compounds would be definitely related to the quality of light utilized in their synthesis. Therefore, plants utilizing strong ions would be expected to require strong light which would synthesize organic compounds with corresponding bond-energy values. These compounds would be expected to supply a corresponding quality of energy to animals in digestive and oxidation processes. Plants utilizing weaker ions and a relatively low quality of light in photosynthesis would be expected to supply a correspondingly low quality of energy to animals.

SUMMARY

The energy properties of plant nutrients are very useful in studying problems of soil fertility and plant nutrition. The average quantities of the different elements found in a wide variety of plants and the relative strength of ions are very closely correlated. The nutrient content of plants and the relative strength of ions seem to be much more closely correlated than are the nutrient content and the concentration of ions in the nutrient medium, as expressed in the percentage saturation of soil colloids.

That the chemical composition of specific plants may vary widely from the average of a large number suggests selective absorption and selective exclusion of certain combinations of elements by some plants. Certain of the selective processes of cultivated plants may be considered as related to phylogenetic tolerance mechanisms to protect the plant from excessive quantities of given elements. The selective accumulation of nutrients by plants seems to be correlated with the inactivation of the excess elements in insoluble compounds, such as in the formation of malates, oxalates, pectates, and other relatively low energy value organic compounds capable of neutralizing excessive cations that may have been present in the native habitat of the plant. Some of the crops in the legume, mallow, and night-shade families selectively accumulate Ca and Cl and selectively exclude Si.

The selective exclusion tolerance mechanism existing in some plants seems to be very different from the selective accumulation mechanism. Plants in the grass family seem to accumulate K and Si and selectively exclude Ca. The selective exclusion of Ca by carbonaceous crop plants may be related to lack of capacity to maintain an abundant supply of CO_2 available for carbohydrate synthesis in the presence of excessive quantities of Ca. By excluding the Ca, the plant may maintain a more favorable supply of CO_2 for photosynthesis.

The varying quantities of the different nutrients and the large number of elements found in crop plants suggest the desirability of considering a more complete nutrient supply in our fertilizer program. The conventional N, P, and K fertilizer combinations are often very inadequate on a number of the humid climate, heavily fertilized soils utilized for production of fruits, vegetables, and other crops of high acreage value.

It seems highly probable that some of the functions of the different plant nutrients are related to their energy properties and to their capacity to enter into oxidation-reduction reactions at definite energy levels. The exothermic reactions in the formation of certain nutrient compounds are in close agreement with the absorption bands in chlorophyll or with the endothermic reactions in photosynthesis. The quality of the radiant energy utilized by plants in the photosynthetic reactions may be related to the quality of the food compounds synthesized. Plants using relatively strong light, or the shorter wave length, may synthesize organic compounds that will supply a comparable quality of energy in oxidation and digestion.

The quality of the energy required in reduction and in assimilation of the nutrient anions varies widely. Synthesis of N can apparently take place at a relatively low energy level as compared with C and P. The specialization in N fixation by soil organisms not exposed directly to radiant energy in sunlight and the efficient assimilation of C by higher plants with a special structure to utilize radiant energy illustrate two assimilation reactions at very different energy levels. P and F, which are the principal anion materials in bones, very probably require a higher quality of energy in their assimilation than does C.

Production of proteinaceous and carbonaceous crops may be related to the relative quantities of N and C available in plants for assimilation. The selective exclusion of Ca by some of the carbonaceous crops may be related to capacity of Ca to lower the availability of CO_2 in the plant.

The selective accumulation of Mg and P in seeds, fruits, tubers, roots, and other storage tissues concerned with reproduction of the plant may be related to the energy stability of the P compounds. $(Mg)_3(PO_4)_2$ is probably the most stable compound that could be readily assimilated by the energy available in respiration and oxidation reactions.

The overvoltage values encountered in electrochemistry suggest that one of the principal functions of the minor nutrient elements may be to increase the decomposition voltage of aqueous solutions. These values suggest that there may be a differential in the relative discharge potential of H and O in combination with different metals. Certain metals may increase the discharge potential of H^+ and enable these ions to enter into organic combinations at a higher energy level than would be possible at the theoretical discharge potential of 1.23 volts for H_2O with simultaneous liberation of H_2 and O_2. The overvoltage values for O would also very probably result in entry of the O into combinations at a higher energy level than when discharged as a gas at the theoretical decomposition voltage for H_2O.

Seemingly, the energy properties will have to be considered in understanding some of the specific functions of plant nutrients. Acceptance of the hypothesis that the energy properties of nutrients affect the intensity of their absorption and the energy required in their assimilation would logically suggest many other phenomena concerned with organic synthesis and nutrition, such as the quality of radiant energy required in assimilation of ions of different strengths and the food value of organic compounds synthesized by the various qualities of energy.

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AN EXPERIMENTAL EVALUATION OF ION-EXCHANGE RELATIONSHIPS[1]

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In a recent examination of the theory of ion-exchange equations for clays and synthetic resins (4) it was concluded that an expression based on the statistical thermodynamics of Guggenheim (2) and adapted for ion-exchange materials by Krishnamoorthy, Davis, and Overstreet (3) was the most general and satisfactory from the theoretical standpoint. In the present research, a number of the ion-exchange formulations that have been proposed were subjected to experimental test.

Since ion-exchange equations are equilibrium expressions, it was judged inappropriate to test them experimentally with adsorbents in which the ion-exchange process is irreversible or in which equilibrium conditions do not prevail. Also, it was thought probable that valid results could not be obtained with substances composed of mixtures of widely different types of adsorbents.

With these considerations in mind, experimental materials were selected that were believed to be mineralogically pure or were characterized by a single class of active groups. Moreover, by preliminary experiments it was ascertained that conditions of complete equilibrium and reversibility of the exchange reactions prevailed for all of the ions studied. Also, since radioactive isotopes (K^{42}, Rb^{86}, Cs^{137}, and La^{140}) were employed in many of the studies, it was made certain that complete *isotopic* equilibrium was attained for all ions concerned.

The substances selected on the basis of the foregoing conditions consisted of one bentonite, three synthetic resins, and three soil colloids. The ion-exchange equations receiving special consideration were those of Vanselow (5), Gapon (1), and the one based on the theory of Guggenheim (3) and referred to in this paper as the "statistical equation."

EXPERIMENTAL MATERIALS AND METHODS

The natural bentonite used in the investigation was a sample[2] from Utah. It has an exchange capacity of about 130 me. per 100 gm. oven-dry material. The silica-sesquioxide ratio as determined by fusion analysis of the $<1\ \mu$ fraction is 4.20. The dehydration curves and differential thermographs are characteristic of a typical montmorillonite mineral. The flocculation properties of the material are excellent; a 0.1 *S* concentration of CsCl or a 0.5 *S* concentration of LiCl flocculates a 1 per cent suspension of the clay completely.

[1] Taken from a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of doctor of philosophy in soil chemistry, 1949.

[2] Obtained through Prof. D. W. Thorne of the Agricultural Experiment Station at Logan, Utah.

The synthetic resins used[3] were "IR 1," "IR 100," and "Ion X." The resin IR 1 contains SO_3H, COOH, and OH groups; IR 100 contains SO_3H and OH groups; and Ion X contains SO_3H groups only. By titrating the hydrogen forms of IR 1 and IR 100 to pH 7.0, only the SO_3H and COOH groups can be saturated and the phenolic groups are essentially nonfunctional.

In addition to the aforementioned materials, clays from the Yolo, Hanford, and Aiken soil series were used to make the investigation more general. The x-ray diffraction patterns of the Yolo clay show it to be predominantly montmorillonitic. On the same basis Hanford clay is of the hydrous mica type and Aiken clay is kaolinitic in character.

In the preparation of the clay suspensions, particles of less than 1 μ size were obtained by sedimentation methods, flocculated by electrodialysis, and then treated with H_2O_2 to remove the organic matter. The organic-matter–free clay was then electrodialyzed until the cathode chamber gave only a slight test for bases. The H-clay thus prepared constituted a stock suspension. Clays containing a given ion in the adsorbed state were prepared by adding the chosen cation as the hydroxide. In the case of the bentonite, which contained very little organic matter, the H_2O_2 treatment was omitted.

Preparation of the synthetic resin samples differed somewhat from the procedure adopted for the clay and bentonite suspensions. Since the resins are very coarse and can be easily washed, the hydrogen form of the resin was prepared in every case by repeated treatment with 5 N HCl until all adsorbed cations had been replaced by H. Following this, the resin was repeatedly washed with water until free from HCl. Other forms of the resin were prepared from the H-form by neutralization with the required bases so that the resulting resin was approximately 95 per cent saturated with the desired ions.

For the exchange experiments, known volumes of clay suspensions or given weights of resin were added to solutions containing the desired electrolytes. The final volume in almost all cases was made up to 100 ml. The mixture was then equilibrated by shaking for 48 hours. Although preliminary experiments showed that almost complete equilibrium (99 per cent) was attained in a few minutes, the 48-hour period was adopted as further assurance. The equilibrated suspensions were then centrifuged. The suspensions were never filtered through papers or porcelain candles because of possible uptake of ions by the paper or candles. The supernatant liquids were analyzed by accepted procedures, and the amounts of ions remaining adsorbed on the exchange materials were obtained by difference.

Where radioactive isotopes were used, the results were corrected for mass absorption and coincidence errors. The mass absorption corrections were considerable for the soft radiations of Ca^{45} but were not important for the energetic radiations of K^{42} and La^{140}.

In the calculation of equilibrium constants the amounts of ions at equilibrium were all expressed in terms of milliequivalents per 100 ml. The quantities

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[3] The resins IR 1 and IR 100 were obtained from Rohm and Haas Company, The Resinous Products Division, Washington Square, Philadelphia 5, Pennsylvania. The substance Ion X is the resin Dowex 50, 20–40 mesh, manufactured by the Dow Chemical Company, Midland, Michigan.

$[C_A + C_B + C_C \cdots]$ and $[q_A C_A + q_B C_B + \cdots]$—terms which occur in Vanselow's equation and in the equation based on Guggenheim's statistics—were expressed in terms of millimols per 100 ml. With the exception of these two terms, the equilibrium constant is independent of the units in which the concentrations are expressed.

Wherever necessary, the exchange constant between a pair of ions has been corrected for the activity of the ions in solution by means of the principle of ionic strength. For ions of equal valency and where the ionic strength is not greater than 0.05, this correction is often negligible, amounting to only a few per cent.

EXPERIMENTAL RESULTS

The most simple ion-exchange system is one that contains a single pair of monovalent cations only. All exchange equations proposed so far became identical for a monovalent–monovalent ion pair and assume the form

$$k_{AB} = \frac{A(ad)}{A^+} \cdot \frac{B^+}{B(ad)} \cdot \frac{\gamma \pm^2 (B\ \mathrm{Cl})}{\gamma \pm^2 (A\ \mathrm{Cl})}$$

where the suffix (*ad*) refers to the adsorbed state and the $\gamma \pm$ values are the mean activity coefficients of the salts of the two ions in solution.

The foregoing constant for a number of monovalent–monovalent ion pairs was determined for the experimental materials selected. In all cases the relationship was obeyed regardless of how the equilibrium was approached; that is, either by starting with pure $A(ad)$ and adding B Cl or by starting with pure $B(ad)$ and adding A Cl. In these studies 1 to 2 me. of the adsorbent was equilibrated with 0.1 to 5 me. of electrolyte in 100 ml. A summary of the constants obtained is given in table 1. In the table the constants are calculated with reference to ammonium ion; that is

$$k = \frac{A^+(ad)}{(A^+)} \cdot \frac{(\mathrm{NH}_4^+)}{\mathrm{NH}_4\,(ad)}$$

where the terms in parentheses denote activities and all other terms refer to concentrations measured either as millimoles or as milliequivalents per unit volume. Specifically the constants pertain to the reaction

$$\mathrm{NH_4\text{-}clay} + A\ \mathrm{Cl} \rightarrow A\text{-}\mathrm{clay} + \mathrm{NH_4Cl}$$

In the case of divalent–divalent ion pairs the different ion-exchange theories result again in the same expression, which is very similar in form to that for monovalent–monovalent pairs. A number of such reactions were studied by adding divalent cations as the chlorides to the calcium form of the adsorbent. The values for the constant,

$$k = \frac{A(ad)}{(A^{++})} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}\,(ad)}$$

are presented in table 2.

TABLE 1

Values of the constant $k = \frac{A(ad)}{(A^+)} \cdot \frac{(NH_4^+)}{NH_4(ad)}$ *for various monovalent cations and a number of adsorbents*

ADSORBENT	CLASS	CATION A^+	k
Utah bentonite	Aluminosilicate	Li	0.042
		Na	0.21
		K	1.29
		Rb	3.19
		Cs	14.60
		Ag	0.36
Yolo clay	Aluminosilicate	Na	0.30
		K	1.01
		Rb	2.34
		Cs	8.40
Hanford clay	Aluminosilicate	Na	0.17
		K	1.15
		Rb	3.30
Aiken clay	Aluminosilicate	Na	0.195
		K	1.85
		Rb	3.60
IR 1	Synthetic resin	Li	0.46
		Na	0.69
		K	1.06
		Rb	1.41
		Cs	2.13
IR 100	Synthetic resin	Li	0.30
		Na	0.53
		K	1.03
		Rb	1.66
		Cs	3.45
Ion X	Synthetic resin	Li	0.58
		Na	0.78
		K	1.05
		Rb	1.28
		Cs	1.65
		Ag	3.70

For monovalent–divalent ion pairs, the base-exchange equations do not have the same form. That is, for an exchange reaction between NH_4 and Ca, for example, the equations are as follows:

Gapon: $$k = \frac{NH_4\,(ad)}{(NH_4^+)} \cdot \frac{(Ca^{++})^{\frac{1}{2}}}{Ca\,(ad)}$$

$$\text{Vanselow:}\quad k = \frac{\mathrm{NH_4}\,(ad)^2}{(\mathrm{NH_4^+})^2} \cdot \frac{(\mathrm{Ca^{++}})}{\mathrm{Ca}\,(ad)\,[\mathrm{Ca}\,(ad) + \mathrm{NH_4}\,(ad) + \cdots]}$$

$$\text{Statistical:}\quad k = \frac{\mathrm{NH_4}\,(ad)^2}{(\mathrm{NH_4^+})^2}\,\frac{(\mathrm{Ca^{++}})}{\mathrm{Ca}\,(ad)[1\tfrac{1}{2}\,\mathrm{Ca}\,(ad) + \mathrm{NH_4}\,(ad) + \cdots]}$$

where the quantities in parentheses denote activities.

These equations have been derived from different assumptions concerning the "activities of ions" in the adsorbed state. To test them, it is desirable to adjust the experimental conditions so that the proportions of the adsorbed ions will vary over a wide range. In general, the monovalent ions commonly studied, such as Na, NH_4, K, are much less strongly adsorbed than the divalent ions. Because of this it is difficult in some cases to increase the amounts of $NH_4(ad)$, for example, beyond a certain point without using an excessively high concentration of the corresponding salt. If a monovalent ion, the adsorption energy of which is equal to or greater than that of the divalent ion, is employed, however, it is possible experimentally to cover the range of, say, 5 to 95 per cent saturation of the adsorbent with respect to the monovalent ion. For clay and bentonite systems, Rb and Cs ions have the required adsorption energies. For the resin IR 100, K ion can be used successfully.

TABLE 2

Values of the constant $k = \frac{A(ad)}{(A^{++})} \cdot \frac{(Ca^{++})}{Ca(ad)}$ *for divalent cations and a number of absorbents*

ADSORBENT	CLASS	CATION A^{++}	k
Utah bentonite	Aluminosilicate	Mg	0.92
		Sr	1.10
		Ba	1.24
		Cu	0.88
		Pb	1.40
Yolo clay	Aluminosilicate	Mg	0.70
		Sr	1.35
		Ba	1.80
IR 100	Synthetic resin	Mg	0.52
		Sr	1.80
		Ba	3.10
Ion X	Synthetic resin	Mg	0.40
		Sr	2.50
		Ba	5.40
		Pb	4.00
		Mn	0.44
		Zn	
		Cu	

With the foregoing considerations in mind, a series of Cs–Ca equilibria were studied for the Utah bentonite and the K–Ca equilibrium was investigated for the resin IR 100. The results together with the constants calculated according to the various equations are presented in tables 3 and 4. A compilation of the constants calculated by means of Guggenheim's statistical theory for the NH_4–Ca pair on various adsorbents is presented in table 5.

TABLE 3

Ca–Cs equilibrium data on Utah bentonite $< 1\ \mu$

1 gm. clay = 1.025 me. used in each case. [Ca(*ad*) + H(*ad*) + Cs(*ad*)] and [1½ Ca(*ad*) + H(*ad*) + Cs(*ad*)] are expressed as millimols per 100 ml. All other concentrations are expressed as milliequivalents per 100 ml.

Cs(*ad*)	Cs^+	Ca(*ad*)	Ca^{++}	Ca(*ad*) + H(*ad*) + Cs(*ad*)	1½ Ca(*ad*) + H(*ad*) + Cs (*ad*)	$\frac{\gamma \pm^3 CaCl_2}{\gamma \pm^4 CsCl}$	*k* STATISTICAL	*k* VANSELOW	*k* GAPON*
.1575	.0425	.820	0.624	.616	.821	.843	10.74	13.73	5.05
.232	.068	.754	0.690	.648	.837	.836	10.65	13.74	5.32
.303	.097	.686	0.758	.684	.855	.832	10.48	13.10	5.61
.371	.129	.616	0.828	.725	.879	.828	10.48	12.71	5.92
.436	.164	.548	0.896	.752	.889	.824	10.71	12.67	6.19
.503	.197	.488	0.956	.785	.904	.821	11.05	12.80	7.24
.560	.240	.434	1.010	.810	.918	.817	11.18	12.67	7.64
.612	.288	.382	1.062	.836	.931	.814	10.74	11.96	8.11
.662	.338	.332	1.112	.862	.944	.812	11.05	12.13	8.80
							10.78±0.21	12.84±.46	

* Uncorrected for activity coefficients of ions in solution.

TABLE 4

Results of Ca–K *equilibrium data on IR 100*

1 gm. resin = 1.72 me. used in each case. [Ca(*ad*) + H(*ad*) + K(*ad*)] and [1½ Ca(*ad*) + H(*ad*) + K(*ad*)] are expressed as millimols per 100 ml. All other concentrations are expressed as milliequivalents per 100 ml.

K (*ad*)	K^+	Ca(*ad*)	Ca^{++}	Ca(*ad*) + H(*ad*) + K(*ad*)	1½ Ca(*ad*) + H(*ad*) + K(*ad*)	$\frac{\gamma \pm^3 CaCl_2}{\gamma \pm^4 KCl}$	*k* STATISTICAL	*k* VANSELOW	*k* GAPON*
.458	.542	0.575	.0128	1.432	1.576	.800	8.08×10^{-3}	8.88×10^{-3}	.188
.244	.256	0.771	.0130	1.334	1.527	.810	8.12×10^{-3}	9.32×10^{-3}	.161
.173	.325	1.008	.052	1.216	1.464	.797	7.97×10^{-3}	9.56×10^{-3}	.121
.117	.383	1.150	.175	1.145	1.432	.789	7.91×10^{-3}	10.20×10^{-3}	.111
.089	.411	1.213	.377	1.113	1.417	.777	8.00×10^{-3}	10.18×10^{-3}	.110
.067	.433	1.316	.810	1.064	1.393	.758	8.20×10^{-3}	10.54×10^{-3}	.106
							$(8.05 \pm .008) \times 10^{-3}$	$(9.78 \pm 0.50) \times 10^{-3}$	

* Not corrected for activity coefficients of ions in solution.

For the monovalent–trivalent ion pairs the exchange equations agains show differences in form. For example, for the Cs–La pair,

Gapon:
$$k = \frac{\text{Cs}\,(ad)}{(\text{Cs}^{+})} \cdot \frac{(\text{La}^{+++})^{1/3}}{\text{La}(ad)}$$

Vanselow:
$$k = \frac{\text{Cs}\,(ad)^{3}}{(\text{Cs}^{+})^{3}} \cdot \frac{(\text{La}^{+++})}{\text{La}\,(ad)\,[\text{La}\,(ad) + \text{Cs}\,(ad) +}$$

Statistical:
$$k = \frac{\text{Cs}\,(ad)^{3}}{(\text{Cs}^{+})^{3}} \cdot \frac{(\text{La}^{+++})}{\text{La}\,(ad)\,[2\text{La}\,(ad) + \text{Cs}\,(ad) + \cdots]^{2}}$$

Here, as with monovalent–divalent equilibria, the choice of ions is important in testing the equations. Only those monovalent ions the adsorption affinities of which are very large are useful.

Attempts to study the Cs–La equilibrium at pH values near 7.0 were unsuccessful because in this range of pH, La either is precipitated in the mass of the adsorbent or exists partly in the form of ions of valencies less than +3. In other words, if La is assumed to exist as a trivalent ion, the equivalents of La adsorbed exceed the equivalents of Cs released. On the other hand, it was found that at pH values of 3.0 and below lanthanum behaves normally as a trivalent ion. Because of this, the Cs–La equilibria were investigated by adding LaCl_3 and CsCl to the hydrogen form of the adsorbent in such a way that the pH of the mixture was below 3.0. These experiments had the disadvantage that wide variations in Cs(*ad*) and La(*ad*) were unattainable. The results for Utah bentonite and IR 100 are given in tables 6 and 7.

TABLE 5

Values of the constant $k = \frac{NH_4(ad)^2}{(NH_4^{+})^2} \cdot \frac{(\text{Ca}^{++})}{\text{Ca}(ad)\,[1\tfrac{1}{2}\,\text{Ca}(ad) + \text{NH}_4(ad) + \ldots]}$ *for various absorbents*

ADSORBENT	CLASS	k
Utah bentonite	Aluminosilicate	.044
Yolo clay <1μ	Aluminosilicate	.090
Hanford clay <1μ	Aluminosilicate	.085
Aiken clay <1μ	Aluminosilicate	.184
IR 100	Synthetic resin	.0070
Ion X	Synthetic resin	.0026

In most of the studies described thus far (Cs–La experiments excepted), only the pair of cations under consideration were present in appreciable amounts in the adsorbent and aqueous phases. A series of experiments were conducted to study the influence of a third or fourth cation on the exchange constant of a given pair. That is, the equilibrium constant between Cs and Ca was determined in the presence of large amounts of H, Na, K, and Ba ions. The results together with the equilibrium constant calculated according to the three equations are presented in table 8. The values for the equilibrium constant in the table may be compared with those of table 3.

TABLE 6

Results of the Cs–La *equilibrium on Utah bentonite* $<1\mu$

1.5 gm. clay = 1.93 me. used in all cases. [La(*ad*) + Cs(*ad*) + H(*ad*)] and [2 La(*ad*) + Cs(*ad*) + H(*ad*)] are expressed as millimols per 100 ml. All other concentrations are expressed as milliequivalents per 100 ml.

Cs(*ad*)	Cs^+	La(*ad*)	La^{+++}	La(*ad*) + Cs(*ad*) + H(*ad*)	2 La (*ad*) + Cs(*ad*) + H(*ad*)	$\frac{\gamma \pm^4 LaCl_3}{\gamma \pm^6 CsCl}$	*k* STATISTICAL	*k* VANSELOW	*k* GAPON*
.339	.129	.0971	.0071	1.865	1.900	.890	.330	.346	5.20
.320	.148	.180	.0214	1.804	1.867	.868	.283	.304	3.33
.304	.164	.266	.0462	1.760	1.845	.861	.293	.307	2.51
.295	.173	.338	.0784	1.706	1.818	.852	.250	.283	2.16
.284	.184	.403	.1181	1.662	1.796	.841	.276	.320	1.88
.275	.193	.462	.1635	1.622	1.776	.838	.272	.334	1.56
.268	.200	.509	.220	1.590	1.761	.823	.277	.337	1.59
.261	.207	.543	.291	1.570	1.751	.806	.283	.352	1.54
.256	.212	.590	.348	1.538	1.734	.804	.278	.352	1.44
.251	.217	.625	.417	1.514	1.722	.797	.277	.367	1.38
.246	.222	.655	.491	1.492	1.711	.788	.274	.361	1.34
.241	.227	.675	.575	1.480	1.705	.780	.274	.363	1.31
							.274±.006	.335±.023	

* Uncorrected for activity coefficients of ions in solution.

TABLE 7

Results of the Cs–La *equilibrium on IR 100*

1 gm. resin = 1.72 me. [La(*ad*) + Cs(*ad*) + H(*ad*)] and [2 La(*ad*) + Cs(*ad*) + H(*ad*)] are expressed in millimols per 100 ml. All other concentrations are expressed as milliequivalents per 100 ml.

RESIN	Cs(*ad*)	Cs^+	La(*ad*)	La^{+++}	La(*ad*) + Cs(*ad*) + H(*ad*)	2 La(*ad*) + Cs(*ad*) + H(*ad*)	$\frac{\gamma \pm^4 LaCl_3}{\gamma \pm^6 CsCl}$	*k* STATISTICAL	*k* VANSELOW	*k* GAPON*
me.										
1.72	.692	.324	0.521	0.45×10^{-3}	1.372	1.546	.815	2.86×10^{-3}	3.65×10^{-3}	.314
1.72	.373	.389	1.036	7.0×10^{-3}	1.030	1.375	.800	2.53×10^{-3}	4.51×10^{-3}	.177
1.72	.110	.398	1.222	0.341	0.906	1.313	.772	2.64×10^{-3}	5.54×10^{-3}	.159
1.72	.090	.418	1.330	0.775	0.854	1.287	.742	2.60×10^{-3}	5.90×10^{-3}	.149
0.43	.036	.472	0.281	0.220	0.242	0.336	.830	2.56×10^{-3}	4.92×10^{-3}	.164
0.86	.182	.326	0.501	0.45×10^{-3}	0.526	0.693	.849	2.78×10^{-3}	4.81×10^{-3}	.088
								$(2.71\pm.12) \times 10^{-3}$	$(4.88\pm0.56) \times 10^{-3}$	

* Uncorrected for activity coefficients of ions in solution.

On the basis of theoretical considerations described in a later section, it was concluded that in the case of adsorbents which are mixtures of two or more pure ion-exchange substances, exchange constants would not be obtained for any ion pair even though the individual components of the adsorbent mixture give a good constant for a pair of ions. To demonstrate this, a mixture of Yolo and Aiken clays (in a constant ratio) and a mixture of Utah, Yolo, and Aiken clays and IR 1, IR 100, and Ion X (in a constant proportion) were prepared. The ion-exchange constants in these preparations were then determined for the NH_4–Ca and Na–NH_4 ion pairs. The results are given in tables 9 and 10.

TABLE 8

Influence of other ions (adsorbed or free) on the equilibrium constant between Cs and Ca on Utah bentonite

Equilibrium amounts of ions given in terms of milliequivalents per 100 ml. Amount of clay used for each system = 2.5 gm. per 100 ml. = 3.153 me. per 100 ml.

	H-CLAY + $CaCl_2$ + CsCl	Na-H-CLAY + $CaCl_2$ + CsCl	H-K-CLAY + $CaCl_2$ + CsCl	H-Ba-CLAY + $CaCl_2$ + CsCl
Ca(*ad*)	0.462	1.158	0.960	0.660
Cs(*ad*)	0.806	0.922	0.984	0.840
H(*ad*)	1.885	0.633		0.409
Na(*ad*)		0.436		
K(*ad*)				
Ba(*ad*)				1.240
H(*ad*) + K(*ad*)			1.209	
Ca^{++}	1.118	0.320	0.620	0.890
Cs^+	0.194	0.078	0.126	0.160
H^+	1.312	0.020		0.204
Na^+		2.064		
K^+				
Ba^{++}				1.260
$H^+ + K^+$			1.944	
$\frac{\gamma\pm^3(CaCl_2)}{\gamma\pm^4(CsCl)}$	0.795	0.801	0.795	0.788
k_{Cs-Ca}: Statistical	10.93	10.79	10.78	10.92
k_{Cs-Ca}: Vanselow	11.36	12.01	11.70	13.27
k_{Cs-Ca}: Gapon	9.51	5.78	6.40	7.51

TABLE 9

Equilibrium data for the NH–Ca *exchange in mixed systems of Yolo and Aiken clays*

Each contained the following amounts of clays per 100 ml.: 1.175 gm. Yolo clay = 0.705 me.; 7.050 gm. Aiken clay = 2.115 me. All concentrations are expressed in terms of milliequivalents per 100 ml. of suspension

SYSTEM NUMBER	NH_4(*ad*)	NH_4^+	Ca(*ad*)	Ca^{++}	*k** STATISTICAL
1	1.140	2.158	0.313	0.275	0.088
2	0.930	1.568	0.508	0.434	0.112
3	0.780	1.205	0.574	0.543	0.148
4	0.635	0.850	0.804	0.766	0.203

* Not corrected for the activity coefficients of the ions in solution.

Because of the probability that adsorbed H ion in clays and synthetic resins is not completely dissociated, it was concluded in an earlier paper (3) that hydrogen may not behave normally in exchange reactions. That is, none of the exchange equations developed thus far would hold for ion pairs involving H. This question will receive particular attention in a future paper. To illustrate the problem, a series of calculated exchange constants for the H–K pair on IR 100 and on Utah bentonite are presented in tables 11 and 12.

TABLE 10

Equilibrium data for the NH_4–Na exchange in mixed systems, of clays and synthetic resins

Each contained the following amounts of adsorbents per 100 ml.: 0.20 gm. IR 100 = 0.344 me.; 0.20 gm. IR 1 = 0.574 me.; 0.20 gm. Ion X = 0.840 me.; 0.50 gm. Utah bentonite = 0.650 me.; 0.39 gm. Yolo clay = 0.235 me.; 2.35 gm. Aiken clay = 0.705 me. All concentrations are expressed in terms of milliequivalents per 100 ml. of suspension.

SYSTEM NUMBER	$NH_4(ad)$	NH_4^+	Na(*ad*)	Na^+	$k = \frac{Na(ad)}{(Na^+)} \cdot \frac{(NH_4^+)}{NH_4(ad)}$
1	2.06	1.26	0.26	0.24	0.66
2	1.82	1.00	0.50	0.50	0.55
3	1.46	0.86	0.86	1.14	0.45
4	1.16	1.16	1.16	2.84	0.41

TABLE 11

Equilibrium data for the H–K *exchange on IR 100*

1 gm. resin = 1.72 me. used in each case. All concentrations are expressed as me. per 100 ml.

H(*ad*)	H^+	K^+	K(*ad*)	$k^* = \frac{K(ad)}{K^+} \cdot \frac{H^+}{H(ad)}$
1.660	3.192	.0413	.0597	2.85
1.414	1.350	.1510	.3490	2.24
1.189	1.053	.2483	.5517	2.04
1.030	0.690	.296	.704	1.58
0.830	0.890	.857	.943	1.18

* Not corrected for activity coefficients of ions in solution.

TABLE 12

Equilibrium data for the H–K *exchange on Utah bentonite*

2.3 gm. clay = 2.996 me. used in each case. All concentrations expressed as me. per 100 ml.

H(*ad*)	H^+	K(*ad*)	K^+	$k = \frac{K(ad)}{K^+} \cdot \frac{H^+}{H(ad)}$
2.818	.490	.178	0.222	.139
2.611	.385	.385	0.615	.0923
2.506	.490	.490	1.510	.0634
2.281	.715	.715	4.285	.0522

DISCUSSION

As pointed out in the section on "Experimental Results" all of the ion-exchange equations that have been proposed reduce to the same relationship for ions of equal valency. The experiments conducted with monovalent–monovalent and divalent–divalent ion pairs reveal very satisfactory constants for all pairs investigated except those involving hydrogen. This was uniformly true for the bentonite, soil colloids, and synthetic ion exchangers selected for experimentation. Also, as shown in table 8, the constant for a given pair is independent of the presence of other ions in the system. Further, experimental results not presented in this paper show that the exchange constant for a pair of ions is independent of the mass of the adsorbent and the volume of the solution phase.

The data for the monovalent–divalent ion pairs reported in tables 3 and 4 clearly bring out the inadequacy of Gapon's ion-exchange formulation. The formulation of Vanselow and the statistical equation appear to be about equally satisfactory for this type of ion pair. From the data for monovalent–trivalent ion pairs (tables 6 and 7) the defects of Gapon's equation are even more apparent. Also it is evident from these same data that the statistical formulation is appreciably better than that of Vanselow. This comparison is summarized in table 13.

TABLE 13

Maximum variation of exchange constants as calculated according to three different ion-exchange formulations

SYSTEM NUMBER	SYSTEM	STATISTICAL k	VANSELOW k	GAPON k
1	Ca-clay + CsCl	11.22 –10.40	13.21 –12.18	7.77 –5.55
2	Ca-clay + CsCl	11.18 –10.48	13.74 –12.13	8.80 –5.05
3	Ca-clay + RbCl	0.501 – 0.483	0.684 – 0.587	1.32 –1.06
4	Ca-clay + KCl	0.0798– 0.0741	0.113 – 0.100	0.463–0.405
5	Ca-clay + NH_4Cl	0.0449– 0.0430	0.0603– 0.0528	0.414–0.304
6	H-clay + CsCl + $LaCl_3$	0.293 – 0.274	0.363 – 0.304	5.05 –1.31
7	H-clay + CsCl + $LaCl_3$	0.296 – 0.274	0.412 – 0.360	1.48 –1.19
8	H-IR 100 + RbCl + $CaCl_2$	0.0309– 0.0286	0.0385– 0.0311	1.75 –0.63
9	H-IR 100 + CsCl + $LaCl_3$	(2.86 – 2.53)10^{-3}	(5.90 – 3.65)10^{-3}	0.314–0.088

On the basis of the experimental data presented we are led to conclude that the statistical thermodynamic approach of Guggenheim is the more appropriate treatment of the ion-exchange process. On the other hand, although the considerations of Vanselow are entirely different from those of Guggenheim, the end results may not be conspicuously different unless specially designed experiments are carried out.

Strictly speaking, the ion-exchange equations that have been derived are applicable to mineralogically pure samples of clays or to monofunctional synthetic resins. Theoretically, if the equilibrium constant for a given ion pair is k_A for a pure adsorbent A, and k_B for a pure adsorbent B, then in a mixture of adsorbents A and B no satisfactory equilibrium constant can be found for the ion pair. To illustrate, let us imagine that an ion pair X^+ and Y^+ has attained equilibrium between the adsorbent species A and B and an aqueous solution.

Then
$$k_A = \frac{X_A\,(ad)}{(X^+)} \cdot \frac{(Y^+)}{Y_A(ad)} \tag{1}$$

and
$$k_B = \frac{X_B\,(ad)}{(X^+)} \quad \frac{(Y^+)}{Y_B\,(ad)} \tag{2}$$

By definition
$$k_{mix.} = \frac{X_A\,(ad) + X_B\,(ad)}{(X^+)} \cdot \frac{(Y^+)}{Y_A\,(ad) + Y_B\,(ad)} \tag{3}$$

Equation (*3*) cannot be written in terms of k_A and k_B without involving either $X_A(ad)$ and $X_B(ad)$ or $Y_A(ad)$ and $Y_B(ad)$. That is, the value of k_{mix} will depend upon the amounts present in adsorbents A and B and will no longer give a constant independent of them. This conclusion is amply supported by the data of tables 9 and 10 wherein the apparent constants for the ion pairs NH_4–Ca and NH_4–Na are given for mixtures.

Thus a satisfactory equilibrium constant need not be expected for a soil which contains a mixture of minerals that differ widely in their ion-adsorption properties. This presumably might be the case with many secondary or alluvial soils. On the other hand, in a mature primary soil it is likely that the processes of soil formation have resulted in the formation of predominantly a single type of clay mineral or minerals the exchange properties of which are not widely different (*cf.* the montmorillonitic and hydrous mica types). On the basis of these considerations, it must be concluded that earlier work carried out on whole soils to appraise ion-exchange equations should be regarded with reservations.

The data in tables 11 and 12 show that for ion pairs involving H ion satisfactory exchange constants are not obtained even for monovalent–monovalent pairs. This problem will be treated in detail in a later paper. It can be said that other anomalies have been found in unpublished preliminary work by the authors with permutites and stilbite. With these minerals, satisfactory constants are obtained for ion pairs of equal valence, but for pairs of unequal valencies the formulations that have been proposed break down.

The data presented in this paper show that for ion pairs other than those involving H, the formulation based on Guggenheim's theory gives good constants inasmuch as a particular constant does not vary over wide ranges of concentrations of the ions considered, amounts of the adsorbent, and other ions present. A more rigorous appraisal of the exchange constants can be obtained by testing their internal consistency. That is, derived equilibrium constants should be in agreement with those determined by direct experiment. By way of illustration, the constant for the Cs–Rb pair on Utah bentonite has been calculated from various experimental data, as follows:

$k_{\mathrm{Cs-Rb}}$ = 4.59 by addition of CsCl to Rb-clay.
$k_{\mathrm{Cs-Rb}}$ = 4.58 by calculation from $k_{\mathrm{NH_4-Rb}}$ and $k_{\mathrm{NH_4-Cs}}$.
$k_{\mathrm{Cs-Rb}}$ = 4.60 by calculation from $k_{\mathrm{Rb-Ca}}$ and $k_{\mathrm{Cs-Ca}}$.
$k_{\mathrm{Cs-Rb}}$ = 4.47 by calculation from $k_{\mathrm{Rb-La}}$ and $k_{\mathrm{Cs-La}}$.

SUMMARY

The ion-exchange equations proposed by Gapon and Vanselow and an exchange equation based on the statistical thermodynamics of Guggenheim have been subjected to experimental test with one bentonite clay, three soil colloids, and three synthetic resins.

For ion pairs of equal valency, for which all three exchange equations assume identical forms, very satisfactory constants were obtained in all instances except for ion pairs involving hydrogen ion.

For monovalent–divalent ion pairs, Gapon's equation was found to be unsuitable. The equations of Vanselow and that based on Guggenheim's theory proved to be quite satisfactory for this type except for pairs involving hydrogen.

For monovalent–trivalent exchanges, Gapon's equation was found to be wholly inadequate. For monovalent–trivalent pairs not involving hydrogen, Guggenheim's formulation proved to be entirely suitable; somewhat less satisfactory exchange constants were obtained by means of Vanselow's equation.

None of the equations gave satisfactory equilibrium constants for mixtures of adsorbents with widely different exchange properties.

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PHOSPHATE FIXATION IN CALCAREOUS SOILS[1]

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The reactions that take place when phosphate fertilizers are applied to a soil are of scientific and practical value in the production of crops. In calcareous soils, which are representative of the Intermountain Western United States, numerous chemical reactions and physical changes take place that render soluble phosphate fertilizers unavailable for plant use. This conversion of readily soluble phosphate into a comparatively insoluble or less available form has been termed "phosphate fixation." According to McGeorge and Breazeale (3), fixation of phosphates in calcareous soils is due, in many instances, to formation of compounds more basic than tricalcium phosphate, and calcium, as calcium carbonate, is a definite part of the molecule. McGeorge (4) has reported that Arizona soils have a strong fixing power for soluble phosphates because of the large amount of solid-phase calcium carbonate present and the high pH. Hinkle (2) found by chemical analysis that calcareous soils are well supplied with total phosphorus, but that the amount available to the crop during the growing season is often small.

Unpublished work by the University of Idaho indicated that although there was a reduction in availability when phosphate fertilizers were added to calcareous soils, succeeding crops were able to utilize a portion of the phosphate held by the soil. This suggests that "phosphate fixation" in calcareous soils is not so significant a factor of time and placement of fertilizer as in acid soils. Ensminger and Larson (1) found that soils containing 0.5 and less than 1.0 per cent lime showed the lowest response to phosphate fertilization, and the mean response of these soils as compared to the mean response of the soil in the 1.0 and less than 2.0 per cent lime range was highly significant.

Field and greenhouse tests have shown further that phosphate fertilizers having large proportions of water-soluble fractions gave much greater response than those containing a large proportion of their available phosphorus in the citrate-soluble form.

The object of the investigations reported here was to study the following phases of "phosphate fixation" in calcareous soils: (*a*) the degree of so-called fixation or reversion of phosphate fertilizer in calcareous soils; (*b*) the degree to which the fixed or reverted phosphate may become available for crop use; (*c*) the type of phosphate fertilizers best suited for use on calcareous soils.

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[1] Taken in part from a thesis submitted by Glenn C. Lewis to the Graduate School of the University of Idaho in partial fulfillment of requirements for the degree of master of science and based on research supported by a grant from the Simplot Fertilizer Company of Pocatello, Idaho. Idaho Agricultural Experiment Station Research Paper 304.

MATERIALS AND METHOD

The soil selected for this study is classified in the Blackfoot-Aberdeen Area Report (5) as Bannock loam. It was obtained from an unphosphated alfalfa field on an irrigated farm in southeastern Idaho. Chemical analysis showed that the soil contained the equivalent of 6.1 per cent $CaCO_3$, 5 pounds of available P_2O_5 per acre as determined by CO_2 extraction (1), and had a pH of 7.8. The analysis also showed the soil to be low in sodium and magnesium, high in carbonates, and low in sulfates and chlorides.

The phosphate carriers selected for this study were treble superphosphate, single superphosphate, fused tricalcium phosphate, and precipitated tricalcium phosphate (chemical reagent). To provide uniform distribution in the soil, each fertilizer was ground to pass a 48-mm. sieve. It was recognized that grinding these fertilizers would probably result in more rapid fixation, or it might increase the availability of the phosphate as compared to the regular fertilizer materials. The fertilizers, therefore, were all ground to the same fineness so that any difference in fixation would be relative.

To simplify comparison, the different phosphate carriers were divided into two groups: the water-soluble type (treble and single superphosphate) and the citrate-soluble type (fused tricalcium phosphate and precipitated tricalcium phosphate).

INCUBATION STUDIES

The four phosphate carriers at two rates of application, 50 pounds and 100 pounds of either water-soluble or citrate-soluble P_2O_5 per acre, were each thoroughly mixed with 35 pounds of previously mixed and stored soil. Each of the fertilized soils and a check were then brought up to field-moisture capacity and placed in glazed crocks for each incubation period. Incubation refers to the number of days that the soils were maintained at optimum moisture preceding planting to Romaine lettuce. The following incubation periods were included in the study: 0 or no incubation (soil sample taken after mixture with phosphate carrier and before addition of water), 30, 60, and 90 days.

Chemical analysis of incubated soils

Composite soil samples were taken at regular intervals and analyzed for available P_2O_5 by the carbon dioxide method as a means of determining the amount and rate of fixation of the added phosphate carriers. The time intervals selected for making the available phosphorus determinations were as follows:

No incubation—immediately
30-day incubation—immediately, 1, 4, 8, 12, 20, and 30 days
60-day incubation—immediately, 1, 4, 8, 12, 20, 30, and 60 days
90-day incubation—immediately, 1, 4, 8, 12, 20, 30, 60, and 90 days

Availability of phosphorus as influenced by incubation

The available phosphorus remaining in the soil at definite time intervals during incubation was determined by the carbon dioxide method of extraction.

These determinations were made on all three incubation series, and the averages are shown in figure 1. The curve shows the rapid reduction in soluble P_2O_5 within the first 24-hour period and only slight reduction during the next 60 days. This indicates that fixation was rapid, most of it occurring soon after the phosphate fertilizer was applied to the soil and water added. A definite level of available P_2O_5 was established for the 100-pound application of water-soluble type phosphates and a lower level for the 50-pound application. The citrate-soluble type phosphate showed no significant amount of available P_2O_5 over the check, regardless of rate of application.

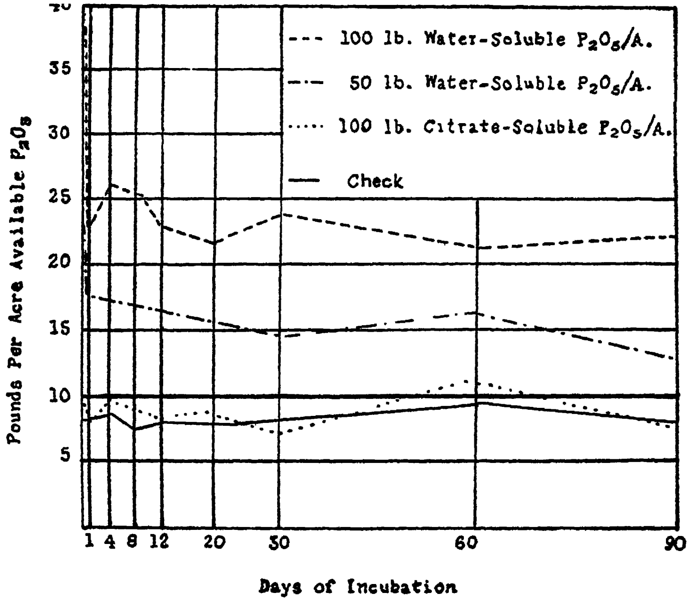

FIG. 1. AMOUNT OF AVAILABLE P_2O_5 REMAINING IN SOIL AFTER DIFFERENT PERIODS OF INCUBATION

PLANT RESPONSE

Methods

Romaine lettuce has been used by Jenny[2] as the indicator plant in determining nutrient levels of soil in greenhouse studies. It had been observed that the amount of growth was determined by the supply of available plant nutrients in the soil. Thus it appeared that the relative growth of Romaine lettuce would be an excellent biological method for determining the availability of phosphate in the soil. Nitrogen and potash were supplied in a nutrient solution so they would not be limiting factors of plant growth.

At the end of the incubation periods, the treated soils were thoroughly mixed.

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[2] Jenny, H. Nutrient Level Determination by Greenhouse Pot Studies. 1944. [Mimeographed.] Division of Soils, University of California.

For each phosphate carrier, rate of application, incubation treatment, and the check, four replications of 1,600 gm. of soil were weighted into 6-inch clay flower pots. Four-week-old Romain lettuce seedlings were then transplanted one to a pot, and water was added.

The plants were grown for 6 weeks without further treatment except for regular watering. They were then harvested, and a composite soil sample was taken from each pot. A second and third crop were planted and handled in the same way. The original treatments of 0, 30-, 60-, and 90-day incubation are used to identify the various soil samples during plant-response studies.

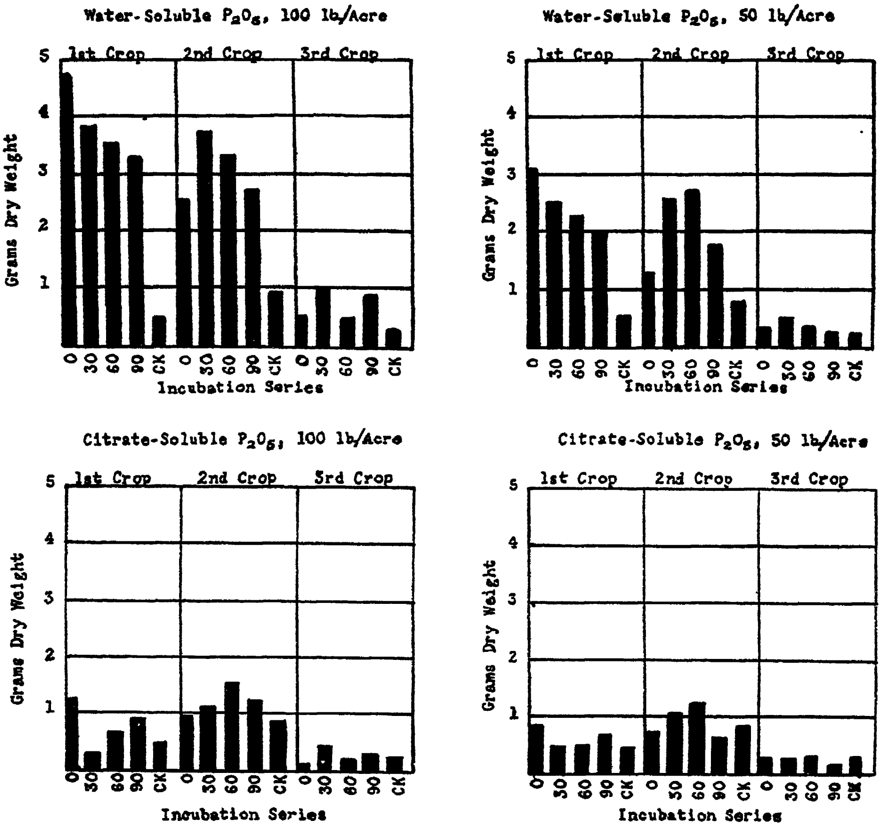

FIG. 2. AVERAGE WEIGHTS OF LETTUCE PLANTS AS AFFECTED BY PHOSPHATE CARRIER IN SOIL, RATE OF APPLICATION, AND INCUBATION TREATMENT

Yield data

Results shown in figure 2 bring out a remarkable correlation with the results obtained by carbon dioxide extraction. The higher yields on the first crops with no incubation when compared with the first crops from the 30- and 60-day incubations indicated a drop in available P_2O_5 after the soil had been incubated and a leveling off where the equilibrium of phosphorus in the soil solution had been established. The yield data on the second and third crops indicated that the supply of phosphorus present was gradually made available and subsequently was utilized by crop growth. The yields decreased with each succeeding crop, but were still higher than those obtained from the checks.

The 100-pound application of available P_2O_5 of the water-soluble type fertilizers showed the greatest plant response, followed by the 50-pound application of the same material, which gave an intermediate response. The 100- and 50-pound applications of available P_2O_5 of the citrate-soluble type fertilizers showed statistically insignificant increase in plant response over the check.

TABLE 1

Utilization of added phosphorus by three crops of lettuce

INCUBATION, DAYS BEFORE PLANTING	TYPE OF FERTILIZER	P_2O_5	PER CENT UTILIZED			
			First crop	Second crop	Third crop	Total
		lb./A.				
0	Water-soluble	100	24.9	11.6	3.9	40.4
0	Water-soluble	50	29.7	13.1	1.5	44.3
0	Citrate-soluble	100	3.7	1.4	2.1	7.2
0	Citrate-soluble	50	4.6	1.0	3.0	8.6
30	Water-soluble	100	19.2	11.6	4.4	35.2
30	Water-soluble	50	19.6	12.5	1.3	33.4
30	Citrate-soluble	100	0.1	0.4	0.1	0.6
30	Citrate-soluble	50	1.1	1.8	0.0	2.9
60	Water-soluble	100	11.9	9.6	3.1	24.6
60	Water-soluble	50	18.3	9.7	2.6	30.6
60	Citrate-soluble	100	1.0	0.6	0.5	2.1
60	Citrate-soluble	50	0.8	0.4	1.8	3.0
90	Water-soluble	100	13.8	10.9	4.7	29.4
90	Water-soluble	50	13.4	8.7	4.1	26.2
90	Citrate-soluble	100	1.4	0.7	0.1	2.2
90	Citrate-soluble	50	0.9	0.0	0.0	0.9

UTILIZATION OF PHOSPHORUS ADDED AS FERTILIZER

The amount of phosphorus a plant can absorb from a fertilized soil is a good index of the availability of the added phosphate. To make such a comparis,on the utilization percentage of the added fertilizer was calculated by subtracting the P_2O_5 (milligrams) taken up by the check plants from the P_2O_5 absorbed by the phosphated plants and dividing the remainder by the P_2O_5 added in the fertilizer. This was done for the three crops of lettuce (table 1).

With the water-soluble fertilizers, between 24.6 and 44.3 per cent of the added phosphate as P_2O_5 was utilized by the three crops of lettuce. The citrate-soluble fertilizer did not release enough available P_2O_5 for the three crops to recover any significant amount of the phosphate added.

AVAILABLE PHOSPHORUS IN SOIL AS INFLUENCED BY CROPPING AND INCUBATION

Soil samples were taken for determining CO_2-soluble P_2O_5 just before transplanting of the first crop, after the first crop, after the second crop, and after the third crop. A portion of the original soil from each treatment was incubated without any crop during the time required to grow the first two crops of lettuce. The results are shown in table 2 for the two rates of phosphate application.

TABLE 2

Phosphorus content of soil by CO_2 extraction

Pounds of available P_2O_5 per acre

INCUBATION PERIOD, DAYS	START PLANT GROWTH	AFTER FIRST CROP	AFTER SECOND CROP	AFTER THIRD CROP	CONTINUOUS INCUBATION NO CROP (8 MONTHS)
I. Check					
0	6.5	7.0	9.5	8.0	10.5
30	6.5	7.0	5.0	8.0	10.5
60	8.0	9.5	5.0	8.0	8.5
90	8.0	8.5	8.0	8.0	8.5
II. Water-soluble type—100 pounds available P_2O_5 per acre					
0	36.5	15.0	13.5	14.3	27.5
30	23.8	14.7	10.5	10.5	27.0
60	21.5	14.7	11.3	12.5	27.0
90	22.7	17.0	15.7	11.5	26.0
III. Water-soluble type—50 pounds available P_2O_5 per acre					
0	17.3	8.3	10.3	13.0	20.3
30	17.5	11.3	9.0	12.5	18.7
60	22.0	12.0	8.3	9.5	15.5
90	13.0	12.7	10.5	10.5	15.5
IV. Citrate-soluble type—100 pounds available P_2O_5 per acre					
0	8.7	12.7	9.0	11.3	12.5
30	5.7	9.0	8.0	10.0	10.0
60	12.7	12.0	6.5	9.0	10.5
90	10.7	14.0	9.0	9.0	10.3
V. Citrate-soluble type—50 pounds available P_2O_5 per acre					
0	11.0	8.0	9.5	8.0	11.5
30	5.0	9.0	7.7	9.5	11.5
60	9.7	11.0	8.3	8.7	9.5
90	7.5	8.0	6.3	8.7	9.5

The CO_2-soluble P_2O_5 in the check soil was very low. The data indicate that incubating the check soil had a tendency to increase the amount of available

P_2O_5 present. Growing a crop did not materially reduce the amount of available P_2O_5 in the unphosphated soil. In incubating the soils before planting, there was an initial reduction in phosphate availability. Continued incubation for 8 months reduced the available P_2O_5 only slightly below the initial reduction. Available soil phosphorus was reduced more by one crop of lettuce than by fixation in the soil. The second crop of lettuce reduced the amount of available P_2O_5 to a lesser degree than the first crop.

The 50-pound addition of available P_2O_5 per acre showed a lower percentage fixation, as would be expected, because there was less available P_2O_5 in the soil than with the 100-pound application, and the third crop of lettuce reduced the available phosphorus almost to that of the check.

Addition of the citrate-soluble types increased the available P_2O_5 very little over that in the unfertilized soils. As a result, neither incubation nor growing three crops had any great effect on the availability of phosphorus in the soil.

DISCUSSION

It was observed during the progress of this work that both the plant and the available P_2O_5 remaining in the soil after fertilizer treatments readily formed themselves into similar groups according to the proportions of water-soluble or citrate-soluble P_2O_5 found in the phosphate carriers. This was substantiated by statistical methods.

Chemical analysis and greenhouse yield data show that when various types of phosphate carriers were added to a calcareous soil, a reduction in availability took place within 24 hours after the fertilizers had been added and that a fairly constant but slightly lower level was maintained throughout the incubation period. This same level was maintained in the soil after 8 months of incubation.

The 100-pound applications of the water-soluble type fertilizers maintained a level of available P_2O_5 at 22 to 25 pounds per acre; 50-pound applications of the same fertilizers maintained a level of 13 to 18 pounds per acre. The citrate-soluble fertilizers gave a level of 8 to 10 pounds per acre, which was not significantly different from the level of the check.

The yield data indicate that the 100-pound application of available P_2O_5 of the water-soluble type fertilizers resulted in the greatest plant growth, followed by the 50-pound applications of the same materials, which gave an intermediate response. The 100-pound and 50-pound applications of available P_2O_5 of the citrate-soluble type fertilizer showed very little increase in plant growth over the check, and this slight increase was not statistically significant.

With the water-soluble type fertilizers, between 24.6 and 44.3 per cent of the P_2O_5 added as fertilizer was utilized by the three crops of lettuce. The citrate-soluble type fertilizers did not produce sufficient available P_2O_5 to give a significant return over the check with the three crops of lettuce.

Levels of available phosphorus in the soil solution can be maintained by additions of water-soluble type fertilizers which will provide sufficient available phosphorus for the plant growth. These levels must be maintained by additions of water-soluble type phosphorus as required.

The rapidity with which the level of available phosphorus is established in calcareous soils when water-soluble type fertilizers are applied indicates that the time of application is less important than it was formerly considered. This study shows that reduction in availability takes place so rapidly that it would be impossible to germinate seeds before this action was largely completed and the phosphorus equilibrium established in the soil.

It is therefore indicated that water-soluble type phosphate fertilizers can be applied in fall or any other season on calcareous soils without further loss of efficiency than would occur if the application immediately preceded crop planting. There probably would be an advantage in adding water-soluble type phosphate fertilizer as a side-dressing to plants already growing, as is shown by the response when seedlings were transferred to soils to which water-soluble type fertilizers had been added and at a time when no incubation had taken place.

The data further indicate that perhaps 15 to 20 times as much of the citrate-soluble type fertilizers would be required to obtain a crop response and an available phosphate level in the soil equivalent to those obtained by the addition of water-soluble type phosphate fertilizer.

SUMMARY

When the various types of phosphate fertilizers were added to the calcareous soils, a reduction in availability took place within 24 hours. The resulting level of available phosphorus in the soil was approximately maintained throughout the incubation period.

The level of available phosphorus maintained in calcareous soils when water-soluble type phosphate fertilizers were added was higher than that maintained by the citrate-soluble types. This was substantiated by determination of available P_2O_5 by the CO_2 extraction method and plant growth response by the Jenny method.

The citrate-soluble type fertilizers did not increase plant growth or significantly raise the available phosphorus level in the soil.

The time of application of the water-soluble type fertilizers, if previous to crop growth, was not important in calcareous soils. Some benefit was shown when more available fertilizer was present during the early stages of growth on soils where no incubation had taken place.

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CAUSES OF THE HIGH NITROGEN AND ORGANIC MATTER CONTENT OF CERTAIN TROPICAL FOREST SOILS

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Many well-drained upland soils in Colombia and Costa Rica are exceedingly rich in total nitrogen and organic matter (1, 2, 3). These observations are perplexing, since nitrogen-climate studies in North America lead one to expect low levels of nitrogen and organic matter in tropical soils.

The present paper attempts to elucidate the causes of the difference in behavior of American north-latitude and of equatorial soils. In principle, the assay is based on an interpretation of nitrogen and organic carbon balances of two tropical and two Californian profiles. Since these four profiles are representative of soils of large areas, the conclusions are believed to possess some degree of generality.

PROFILE INVENTORIES OF NITROGEN AND ORGANIC MATTER

Nitrogen and carbon inventories of four complete profiles are given in table 1. In all profiles the N and C contents of the lowest strata were obtained by extrapolating the N- and C-depth functions to zero value of N and C. In all mineral horizons N and C were determined on the 2-mm. fraction and then adjusted to the stone content of each horizon. The black oak and Ponderosa pine profiles of the Sierra Nevada were on the Shaver Ranch (5,000 feet elevation) about 100 feet apart. They are well drained and on level topography. The two tropical profiles were described previously (1).[2]

In the mineral soil of the oak and pine profiles specks of charcoal could be seen. To assay their influence on the carbon-nitrogen ratio, carbon was determined according to three different methods: dry combustion (2), Schollenberger's hot-wet combustion (4), and Walkley-Black's rapid wet oxidation (5). The conversion factor of the Schollenberger method was 1.18, as previously established (2). The conversion factor of the Walkley-Black method was evaluated on forest floor material and was found to be 1.26 for Ponderosa pine and 1.27 for black oak. Special tests on charcoal pieces from the pine profile showed 13 per cent oxidation by the Walkley-Black method. Commercial wood charcoal was oxidized 7 per cent. According to table 2 the Walkley-Black method yields the lowest values. Accordingly, it was used to compute the carbon contents listed in table 1.

The total nitrogen contents of the tropical profiles are about four to five times as high as those of the Sierran profiles. On an acre basis, the two Colombian profiles average 26,858 pounds of nitrogen. The corresponding value for the Sierran profiles is only 5,731 pounds. It is worth noting that the oak and pine profiles

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[1] S. P. Gessel assisted in collecting the Sierra profiles, and F. T. Bingham determined nitrogen and organic carbon.

[2] The nitrogen content of the forest floor of the Chinchiná profile was erroneously reported (1) as 1.43 per cent N. The correct value is 2.15, as given in table 1.

TABLE 1

Organic matter inventories of two tropical and two Californian soils

All data expressed on oven-dry basis. To convert gm./sq.m. to lb./A., multiply by 8.92.

	APPARENT DENSITY	NITROGEN		ORGANIC CARBON		C/N
		per cent	*gm./sq.m.*	*per cent*	*gm./sq.m.*	
Calima profile (No. 76), Colombia						
Litter fall, 852 gm./sq.m.	....	1.22	10.4	45.87	391(A_c)*	37.6
Forest floor, 504 gm./sq.m.	....	1.75	8.8	44.59	225(F_c)	25.5
0– 2 inches	0.81	1.03	424	20.75	8,538	20.1
2– 8 "	1.05	0.49	784	7.20	11,521	14.7
8–18 "	1.05	0.39	1,040	5.23	13,948	13.4
18–25 "	1.37	0.08	195	0.87	2,119	10.9
25–30 "	1.3	0.03	50	0.20	330	6.7
Total profile	....	....	2,502(N_p)	....	36,681(C_p)	14.7
Chinchiná profile (No. 73), Colombia						
Litter fall, 1,011 gm./sq.m.	....	1.55	15.7	50.44	510(A_c)	32.5
Forest floor, 1,648 gm./sq.m.	....	2.15	35.4	48.24	795(F_c)	22.4
0– 8 inches	1.11	0.78	1,759	10.50	23,683	13.5
8–12 "	1.11	0.64	722	7.09	7,996	11.1
12–16 "	1.06	0.34	366	4.35	4,685	12.8
16–20 "	1.04	0.18	190	2.23	2,356	12.4
20–26 "	0.96	0.14	205	1.80	2,633	12.9
26–50 "	1.0	0.04	244	0.50	3,048	12.5
Total profile	....	....	3,521(N_p)	....	45,196(C_p)	12.8
Shaver-oak profile (No. 23), California						
Litter fall, 155 gm./sq.m.	....	0.82	1.27	48.13	74.6(A_c)	58.7
Forest floor, 4,381 gm./sq.m.	....	0.71	31.1	27.95	1,224(F_c)	39.4
0– 8 inches	0.89	0.11	199	2.41	4,358	21.9
8–16 "	1.04	0.06	127	1.20	2,536	20.0
16–24 "	1.12	0.05	114	0.82	1,866	16.4
24–28 "	1.31	0.04	53	0.40	532	10.0
28–50 "	1.3	0.015	109	0.15	1,090	10.0
Total profile	....	....	633(N_p)	....	11,606(C_p)	18.3
Shaver-pine profile (No. 22), California						
Litter fall, 314 gm./sq.m.	....	0.49	1.54	52.12	164(A_c)	106.4
Forest floor, 18,837 gm./sq.m.	....	0.62	117	34.31	6,463(F_c)	55.3
0– 8 inches	0.84	0.11	188	2.02	3,448	18.4
8–16 "	1.04	0.07	148	1.87	3,952	26.7
16–19 "	0.94	0.06	43	1.25	895	20.8
19–50 "	1.3	0.015	154	0.25	2,559	16.7
Total profile	....	....	650(N_p)	....	17,317(C_p)	26.6

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* N_p and C_p denote total nitrogen and total carbon content of the entire profile. These values are probably accurate within ±2–3 per cent. A_c and F_c represent the carbon content of the litter fall and of the forest floor.

possess, within experimental error, identical amounts of nitrogen. The differences in organic carbon contents of the two pairs of soils are less extreme, the tropical profiles having two to four times as much organic matter.

The distribution patterns reveal marked differences. In Colombia, in spite of the high litter fall, the proportion of carbon in the forest floor to that of the total profile is very small, 0.6 and 1.8 per cent. In the Sierran profiles the carbon content of the oak forest floor amounts to 11 per cent of the total carbon content; for the pine profile the proportion is 37 per cent. In other words, *in the tropics the bulk of the organic matter is inside the mineral soil, whereas in the Sierras a considerable portion rests on top of it.*

DECOMPOSITION CONSTANTS OF SOIL ORGANIC MATTER (ORGANIC CARBON)

Field observations strongly suggest that the forest sites investigated represent stabilized conditions. Soil organic matter appears to have reached a steady state, since profile features are uniform over large areas. Granting the assumption of a near-steady state, we may apply the equilibrium principle, which states that the annual rate of addition of organic carbon is equal to the annual rate of loss, or,

TABLE 2

Comparison of combustion methods

Per cent organic carbon

	OAK PROFILE				PINE PROFILE		
Horizon, *inches*	0–8	8–16	16–24	24–28	0–8	8–16	16–19
Dry combustion	3.70	1.66	1.48	0.65	3.13	2.65	1.92
Schollenberger method	3.52	1.78	1.43	0.68	3.20	2.60	1.91
Walkley-Black method	2.92	1.41	1.01	0.58	2.50	2.21	1.55

$$A_c + R_c = k_c' \left(C_p + A_c + R_c\right) \tag{1}$$

where A_c denotes the carbon added to the soil as litter fall, R_c the carbon added in the form of new roots, C_p the carbon content of the entire profile, including the forest floor. One could readily calculate the constant k_c' if R_c, the annual root production, were known. Ecologists maintain that root growth is related to top growth, but no precise numerical relationship is known. Let us calculate k_c' for various assumed ratios of annual root production and leaf production (litter fall), such as 0.5, 1.0, and 2.0. The true ratio would probably lie somewhere between the extremes of 0.5 and 2.0. The k_c' values calculated for these various ratios are listed in table 3. For the sake of comparison the decomposition rates of alfalfa and of the forest floors also are listed.

The mode of computation is as follows: for Calima, A_c is 391 gm./sq.m. and C_p is 36,681 gm./sq.m., both figures taken from table 1. For a root-leaf ratio of 1.0 the value of k_c' is 391 + 391 divided by 36,681 + 391 + 391, which gives 0.0208, or 2.08 per cent.

The results are striking. Whereas alfalfa and forest litter decompose very rapidly in tropical sites, the loss constants for the entire Calima and Chinchiná profiles are low and of the same order of magnitude as those of the Sierran profiles. This is true irrespective of the assumed root-leaf ratios.

We must conclude that in the two tropical soils, humus—which approximates C_p minus F_c—is not readily oxidized. Inside the soil some property, as yet unidentified,[3] counterbalances the accelerating effect of high temperature and rainfall on the decomposition rates. This retarding factor is not operative in the decay of the forest floor which rests on top of the mineral soil, nor is it active on the buried alfalfa samples, since they do not come into direct contact with the mineral soil particles.

TABLE 3

Annual decomposition constants (k_c') *of organic carbon of total profiles, and related values*

$\frac{R_c}{A_c}$*		COLOMBIA		SHAVER LAKE, CALIFORNIA	
		Calima	Chinchiná	Oak	Pine
0.50	k_c'............*per cent*	1.58	1.11	0.95	1.40
1.00	k_c'............*per cent*	2.08	2.21	1.27	1.86
2.00	k_c'............*per cent*	3.10	3.27	1.89	2.76
Decomposition constant of forest floor (k' for carbon)......*per cent*		63.5	39.1	5.74	2.47
Decomposition of alfalfa....*per cent*		98	90	70	
For $\frac{R_c}{A_c} = 1$..................*years*		143	139	234	160
Annual nitrogen gains† for $\frac{R_c}{A_c} = 1$.................*gm./sq.m.*		17.5	25.3	2.71	4.06
.........................*lbs./A.*		156	226	24	36

* Ratio of annual root production (R_c) to annual litter production (A_c).

† N_p of table 1 divided by years of preceding row.

TIME NECESSARY TO BUILD UP ORGANIC MATTER PROFILES

In a preceding paper (3) an equation was derived which permitted estimation of time functions of forest floor accumulation. In particular, it was shown that dividing the decomposition constant k into the factor 3.0 gives the time necessary to reach 95 per cent of the equilibrium value. If this mode of calculation is applied to the four profiles under consideration, the years listed in table 3 are obtained. Computations were made only for k_c' values corresponding to root-leaf ratios of 1.

These year-values are not accurate. In estimating years it is assumed that k_c' remains constant throughout the building up of the profile. We know, however, that k_c' is not constant. It is higher in earlier than in later stages of carbon accumulation. In table 3, k'_c is the decomposition constant at near-equilibrium. Accordingly, the ages listed are minimum ages.

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[3] In the writer's laboratory, L. Rojas-Cruz found in the Calima profile exceedingly low degrees of calcium saturation.

Although the age figures lack accuracy, nevertheless two significant conclusions of semiquantitative nature may be drawn: First, because of the similarity of the k'_c values for the various regions, it may be inferred that it will take about the same time to build up an organic matter profile in the tropics and in the Sierras. Second, the time necessary to form a stabilized organic matter profile is probably of the order of magnitude of several hundred years, say, more than 200 and less than 1,000 years.

INQUIRY INTO NITROGEN GAINS IN TROPICAL AND TEMPERATE FOREST SOILS

In searching for an explanation of the high nitrogen content of the tropical profiles it would be fallacious to point to the large annual additions of nitrogen as litter fall (table 1). These nitrogen additions cannot be considered real gains. Whereas the carbon in the trees is assimilated from the atmosphere, the nitrogen in the leaves is derived from the soil itself, unless the leaves fix atmospheric nitrogen. A different approach must be sought for evaluating the source of soil nitrogen.

If it takes, say, 300 years to build up the carbon content of a given soil profile, it is safe to assume that it will take about an equal number of years to build up the corresponding nitrogen content. In other words, dividing the total nitrogen content of the profile (N_p in table 1) by the year-values calculated for carbon gives the average annual addition of nitrogen. Results of this sort of calculation also are listed in table 3.

How reliable are these figures is not known because the precise age of the carbon profile is not known. Since the year-values given in table 3 are too low, the calculated nitrogen gains are too high. On the other hand, this method of calculating nitrogen additions implies that during the process of accumulation no nitrogen was lost through leaching or otherwise. The uncertainty of the nitrogen values is therefore considerable. In spite of these limitations it is probably safe to conclude that *the average annual nitrogen gains in the two tropical soils exceed those of the Sierran soils.*

The relatively high nitrogen gains in the two tropical profiles may be attributed to a high addition of nitrogen compounds in the rain water, and to a high nonsymbiotic and symbiotic fixation of atmospheric nitrogen. The author is inclined to stress the latter possibility since he was impressed by the large number of leguminous trees[4].

GENESIS OF ORGANIC MATTER PROFILES IN FORESTS, AND THE ROLE OF FACTORS OF SOIL FORMATION

Let us now try to assemble the factual and deduced information obtained into a coherent picture of soil formation. Though the conclusion will have to be based on four profiles only, it is the author's opinion—which he cannot prove to anyone not familiar with the regions—that the sites investigated are representative of large areas.

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[4] H. L. Mason, Director of the Herbarium of the University of California, who recently visited Colombia, estimates that more than 50 per cent of the forest trees are legumes.

In the warm, humid tropics a bare land surface, such as may exist after deposition of volcanic ash rich in basic minerals, is quickly covered with vegetation. Soil nitrogen builds up rapidly, since it is being added at a high annual rate, presumably as a result of biological nitrogen fixation. This enrichment in soil nitrogen is accompanied by a luxuriant growth of vegetation. Large amounts of litter fall on the ground. The leaves decompose rapidly and, because of the high rainfall, a large proportion of the soluble and dispersible decomposition products (humus) migrate into the mineral soil, as is suggested by the alfalfa decomposition studies and by direct field observation.

In contrast to litter decomposition, the rate of decay of humus inside the mineral soil is slow. Accordingly, the organic matter content of the soil attains high values, and its quasi-equilibrium state is reached within centuries. The nitrogen and carbon depth functions are of sigmoid type (1). The mineral soil continues development, but, in contrast to organic matter formation, at a slow rate. Mineral profile differentiation will affect vegetation only over long periods.

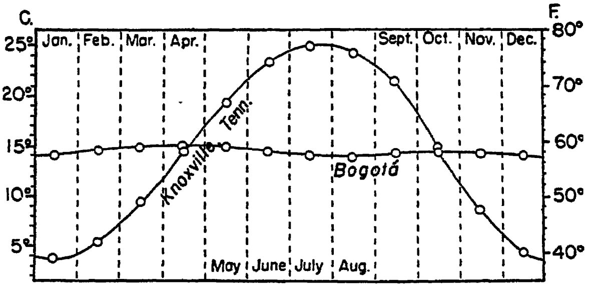

Fig. 1. Seasonal March of Temperature at Bogota, Colombia, and at Knoxville, Tennessee

Both stations have the same mean annual temperature (14.5°C., 58.1°F.)

In the Sierra Nevada of California, soil organic matter accumulation appears to be handicapped by low rates of nitrogen gains. Part of the nitrogen shortage may be attributed to unfavorable climatic conditions, especially the long dry summers, but it can hardly be the whole story. The alfalfa decomposition studies indicate substantial biological activity during the rainy season, especially at lower elevations. Maybe there are not enough leguminous plants in the region studied. At any rate, the general picture portrays nitrogen starvation.

Sierran litter and profile analyses point to a regime of wide carbon-nitrogen ratios, especially in association with pines. Litter production is small and its decomposition is slow. A considerable portion of the organic matter rests on the mineral soil as forest floor. It takes several centuries to build up a stabilized organic matter profile.

The question yet to be answered is whether the frequency of leguminous trees in the tropical forests studied and the related high nitrogen gains are conditioned by equatorial climate or by the history of plant evolution.

The outstanding difference between equatorial and midlatitude climates lies not so much in the annual values of temperature and precipitation as in the invariant seasonal march of temperature, as is illustrated in figure 1. Should further research in the tropical Americas reveal that the high gains of nitrogen and the distribution of legumes are conditioned by the pattern of the seasonal march of temperature, then seasonal climate would have to be proclaimed as the causative soil-forming factor. On the other hand, if the strong leguminous component in the equatorial vegetation is more nearly related to plant evolution and migration, in short, to vegetational history, then the biotic factor of soil formation must be credited with being the principal variable responsible for the high organic matter contents of equatorial soils.

SUMMARY

The formation of profiles high in organic matter in certain tropical regions may be visualized as conditioned by the following factors:

Measurements of litter fall show that production of organic matter is high. Favorable climatic conditions and high annual rates of fixation of nitrogen (legumes) are cited as the primary causes of the luxuriant vegetation.

Decomposition of the forest floor that rests on the mineral soils proceeds at a rapid rate. Observations suggest that a considerable part of the decomposition products infiltrates into the mineral soil.

Decomposition of humus in the mineral soil appears to be slow. Accordingly, humus rapidly accumulates to a high level.

Several hundred years seem to be required to build up soil organic matter to a nearly steady state.

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INFLUENCE OF LEGUMES ON SOIL NITROGEN

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Crop rotation, even where legumes enter the system, may not maintain the nitrogen of some soils. This is evident from data accumulated by the senior author over the last 35 years, and is based on pot and field experiments on irrigated and nonirrigated calcareous soils containing approximately 0.1 per cent of total nitrogen. Moreover such a system may deplete some soils of their plant nutrients more rapidly than a one-crop system in which legumes do not enter. Properly inoculated legumes have the ability under appropriate conditions to utilize atmospheric nitrogen, but they feed by preference upon combined nitrogen. If the total legume is harvested, the soil may be no richer in nitrogen and may be poorer in other nutrients following the legume cropping than it was before. This was found to be the case in a soil containing sufficient nitrogen for the production of near-average crops. The failure of legumes to increase soil nitrogen is due to three factors: (*a*) legumes feed on available nitrogen of the soil and turn to atmospheric nitrogen only if soil nitrogen is reduced to a level where it cannot meet the needs of the growing plant; (*b*) alfalfa reduces soil nitrates to a lower level than do wheat, oats, corn, and many other crops and, hence, drains soil of its total nitrogen; and (*c*) growth of legumes causes a soil to part with its nitrogen more readily than does a nonlegume (1, 2, 3).

The common experience that better crops are obtained following legumes than following nonlegumes raises the question: If legumes do not increase the total plant food of the soil, why do they increase yield? Fallowing does not increase the total nutrients of the soil, yet it increases yield. Probably the main reason is that 2 years' plant food is made available for one crop. This is also true where the legume has been grown. Moreover, alfalfa and possibly other legumes cause soil to part with its nitrogen more readily than do nonlegumes, hence there is an increase in yield of crops following legumes. Such methods for increasing crop yields are sound soil practices, but they must be used with the understanding that the total nitrogen of the soil may not be increased (1).

Data presented in this paper were obtained from a long-time experiment planned to learn the influence of legumes and wheat upon the percentage of nitrogen in a soil where all conditions were carefully controlled and the nitrogen content of the soil was accurately measured.

METHOD OF EXPERIMENTATION

Two-gallon jars were filled with soil from the central experimental farm (Greenville). Approximately 2 kgm. was placed in each jar. The soil had not previously grown legumes and had the composition reported previously by Greaves, Stewart and Hirst (1). It was thoroughly mixed, sieved to remove any rocks or coarse material, remixed and resieved several times, so that each pot contained soil as nearly uniform as possible. The nitrogen content of the soil when placed in the pots was 0.1040 per cent.

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[1] Temporarily withdrawn; resubmitted August 18, 1949.

Some of the pots were fallowed, others seeded with wheat, and still others with the following legumes: alfalfa, crimson clover, cowpeas, Canadian field peas, soybeans, garden beans, or lupines. Half of the pots were planted with inoculated seed, the other half with uninoculated seed. Crops were grown to maturity in the vegetation house; harvested by digging up the plants and separating them into leaves, stalks, and roots; weighed; and analyzed for total nitrogen. The crops on half the pots were returned to the soil and those on the other half were removed. Hence, each legume entered into the following system, each treatment represented by three pot samples:

TABLE 1

Effect on nitrogen in soil of 16 years' cropping to alfalfa and wheat

TREATMENT	NITROGEN CONTENT OF SOIL	
	Averages	Loss or gain over fallow
	per cent	*per cent*
Fallow	.1053	
Alfalfa crop returned uninoculated	.1180	.0127
Alfalfa crop removed uninoculated	.1050	−.0003
Alfalfa crop returned inoculated	.1181	.0128
Alfalfa crop removed inoculated	.1080	.0027
Wheat crop returned	.1056	.0003
Wheat crop removed	.0955	−.0098
5% level of significance	.0050	.0050
1% level of significance	.0069	.0069

Legume uninoculated, crop removed from soil.
Legume uninoculated, crop returned to the soil.
Legume inoculated, crop removed from the soil.
Legume inoculated, crop returned to the soil.

The wheat crop removed from and that returned to the soil also involved three pot samples each.

During the experiment the pots were shifted from place to place to equalize temperature and other variations. At the end of 16 years each soil was transferred into a large container, thoroughly ground, mixed, and sampled. Duplicate nitrogen determinations were made on the soil from each pot. The data presented in the present paper are averages from such analyses at the close of 16 years of cropping. On each legume statistics were calculated to determine significance of variance between treatments, variations within pot samples being used as the error.

EXPERIMENTAL RESULTS

Average percentages of nitrogen in the variously treated alfalfa pots are given in table 1. They are the averages of three pots.

All the inoculated legume plants were nodulated to a greater degree than the uninoculated, but nodulation was not always absent from the uninoculated. The nitrogen content of the soil in the fallow pots was used for comparison of changes due to the legumes because of the belief that methods of handling made it a more accurate standard than the analysis obtained at the beginning. Growth of alfalfa on this soil for 16 years and removal of crop did not significantly increase the soil nitrogen over that in fallow soil. This is true even though the alfalfa was properly inoculated. Returning the crop to the soil resulted in a highly significant increase in soil nitrogen. This increase, calculated to the acre-foot basis for the 16 years, was 450 pounds, or an annual average gain of 28 pounds an acre. Undoubtedly, under field conditions a greater gain would occur as (*a*) the yield in the greenhouse was exceptionally low, never more than 1 ton per acre; and (*b*) there may have been some loss in nitrogen due to bacterial decomposition which may have been more rapid in the green-manured soil than in the fallow soil, hence, the gains reported are not maximum. This supposition is borne out in the results reported for the wheat crop. The loss of nitrogen from the wheat soil for 16 crops was 353 pounds, or an annual loss of 22 pounds per acre. This is approximately that removed by the wheat plant, for where the wheat plant was returned to the soil, the soil nitrogen was maintained. The results amply demonstrate that for *this* soil, growth of alfalfa and removal of the crop did not increase soil nitrogen, but growth of alfalfa and its return to the soil resulted in a highly significant gain in soil nitrogen.

TABLE 2

*Effect on nitrogen in soil of 16 years' cropping to various legumes**

TREATMENT	NITROGEN CONTENT OF SOIL											
	Crimson clover		Cowpeas		Field Peas		Soybeans		Garden beans		Lupines	
	Average	Loss or gain over fallow	Average	Loss or gain over fallow	Average	Loss or gain over fallow	Average	Loss or gain over fallow	Average	Loss or gain over fallow	Average	Loss or gain over fallow
	%	%	%	%	%	%	%	%	%	%	%	%
Crop returned uninoculated..	.1105	.0052	.1022	−.0031	.1146	.0093	.1058	.0005	.1116	.0014	.1058	.0005
Crop removed uninoculated	.0992	−.0061	.1020	−.0033	.1019	−.0034	.1028	−.0027	.0999	−.0054	.1015	−.0038
Crop returned inoculated....	.1145	.0092	.1047	−.0006	.1120	.0067	.1132	.0079	.1167	.0063	.1121	.0068
Crop removed inoculated....	.1019	−.0034	.1049	−.0004	.1032	−.0021	.1057	.0004	.1015	−.0038	.0992	−.0061
5% level of significance......		.0054		.0037		.0038		.0036		.0033		.0044
1% level of significance......		.0076		.0052		.0053		.0050		.0045		.0061

* Average nitrogen content of fallow soil used for comparison is 0.1053 per cent.

A significant loss of nitrogen occurred in soil on which uninoculated crimson clover was grown and removed, but where crimson clover was inoculated and returned to the soil, there was a significant increase in soil nitrogen (table 2). Apparently inoculation rendered crimson clover more efficient in increasing soil nitrogen. Crimson clover differed from the alfalfa in that, when removed, it depleted the nitrogen supply of the soil, whereas alfalfa maintained the soil nitrogen at a constant level. These results indicate that crimson clover should be inoculated, but even when inoculated it is not the equivalent of alfalfa as a soil builder. This may be due to the difference in nitrogen content of the two legumes (5). Alfalfa carried 17 to 18.5 per cent protein, whereas crimson clover carried 14.3 to 18.5 per cent protein.

Soil on which uninoculated cowpeas were grown registered a loss of soil nitrogen approaching significance even where the crop was returned to the soil as green manure (table 2). Where cowpeas were inoculated, the soil nitrogen was maintained at the same level as in the fallow. Evidently so far as this soil is concerned, cowpeas are not so good a soil builder as is crimson clover.

Growth and removal of field peas caused a loss of soil nitrogen, whereas returning the total crop to the soil caused a highly significant gain.

Satisfactory gains in soil nitrogen occurred where inoculated soybeans were returned. But where the crop was removed or uninoculated and returned there was no gain.

Data for the garden beans are similar to those obtained for other legumes (table 2). Satisfactory gains in nitrogen occurred where the legume was returned to the soil and losses where the legume was removed. The results in favor of inoculation are highly significant. Inoculation may manifest itself by an increase in yield, an increase in protein content of the legume, or an increase in the soil nitrogen balance. At times only one effect may manifest itself; at other times inoculation may affect the legume in two or more ways. Garden beans manifest all three effects (5).

When lupines were inoculated and the crop was returned, the soil made significant gains in nitrogen, but when uninoculated lupines were turned under no gains in nitrogen occurred. Where uninoculated lupines were grown on this soil and the complete crop was removed, the soil lost nitrogen (table 2).

The results with all legumes substantiate this conclusion: Legumes feed first on soil nitrogen and use atmospheric nitrogen only if soil nitrogen is insufficient to meet the needs of the growing plants.

Leaves, stems, and roots were all harvested in this experiment, the roots being harvested yearly, in contrast with field practices. Even in this work, however, many leaves fell and found their way into the soil. This leaf fall was considerable at times and corresponds to what may occur under field conditions. In field work the roots are returned and may grow for several years. Hence, they may change the root zone. Thus, the results are not directly comparable with field results but, taken in connection with field experiments, make the conclusions highly probable for similar field soils.

The percentage of nitrogen in the roots as compared with the total nitrogen of the legume varied with the legume. It was 6 per cent in Canadian field peas and soybeans, 7 per cent in garden beans, 8 per cent in lupines and cowpeas, 16 per cent in clover, and 40 per cent in alfalfa. The protein content of cowpeas—stems, leaves, and stocks—was less than that of alfalfa and greater than that of crimson clover (5).

Table 3 lists the percentages of total nitrogen in the roots of the legumes and of wheat. There is no evidence of soil gains in nitrogen from growth of alfalfa in the field even where the roots are returned to the soil (4). Hence, it is highly probable that no gains occur in field work where other legumes are grown and the crops removed from the soil. The following conclusion appears justifiable: Soils which contain sufficient nitrogen to produce a fair crop of nonlegumes will not cause measurable gains in nitrogen, if planted to legumes and the legume removed, but when the legumes are plowed under, appreciable gains of nitrogen may occur. Properly inoculated legumes feed first on the combined nitrogen of the soil, and if this is insufficient to meet their needs they draw on the nitrogen of the air. Hence there are two practical methods of maintaining soil nitrogen by use of legumes in crop rotation systems: (*a*) the legume is plowed under and allowed to decay, thus furnishing nitrogen to successive crops, and (*b*) the legumes grown on the soil are fed and the manure is returned to the soil (4).

TABLE 3

Percentages of total nitrogen of legumes and of wheat in roots

CROP	NITROGEN IN ROOTS	CROP	NITROGEN IN ROOTS
	per cent		*per cent*
Canadian field peas	6	Cowpeas	8
Soybeans	6	Clover	16
Garden beans	7	Alfalfa	40
Lupines	8	Wheat	19

SUMMARY

Wheat and several different legumes were grown in pots under controlled conditions and compared with fallow soil. One set of each legume was inoculated, and a duplicate set was uninoculated. In half the inoculated and half the uninoculated sets, the crops were removed from the soil; in the others, the legumes were returned to the soil. The soil was analyzed at the beginning of the experiment and at the end of 16 years.

The following conclusions may be drawn from the work:

Growth of alfalfa for 16 years on the soil used in this experiment and removal of the crop did not measurably increase the total nitrogen of the soil. This was true for both inoculated and uninoculated plants. Where the crop was returned to the soil, a highly significant gain in soil nitrogen resulted. Inoculation of the alfalfa even where the plants were turned under was without effect on the soil nitrogen.

Even properly inoculated legumes feed first on the nitrogen of the soil and turn to atmospheric nitrogen only if the soil nitrogen is insufficient to meet their needs. Hence the growing of legumes on this soil and the removal of the crop, even where the legume was properly inoculated, did not increase the soil nitrogen. Probably there is a certain nitrogen balance in some soils below which legumes may increase the soil nitrogen even where the complete crop is removed; for this soil it is, undoubtedly, below 0.105 per cent.

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BOOKS

The ABC of Soils. By Jacob S. Joffe. Pedology Publications, New Brunswick, New Jersey, 1949. Pp. 383, plates 12. Price $3.80.

The author has prepared something novel in an introductory soils textbook for students in agriculture. It is characterized by a wealth of fundamental information interspersed with information derived from personal experiences of the author. Unlike conventional primary textbooks, there are comparatively few illustrations and tables of data. Instead, the author has filled every page with the maximum amount of useful information. The thorough treatment accorded the climatogenic and intrazonal soil types is unique in an elementary text. Of particular interest in this material are the descriptions of agricultural features in the respective zonal soil areas and the excellent discussion of the saline and organic soils, their natures and methods of handling. The practical side of pedology is also thoroughly discussed under the titles: irrigation, drainage, liming, fertilizers, and working the land. In his treatment of these subjects, the author significantly relates many of the practices to the inherent characteristics of the soil profile, something no previous American author has attempted. The author expresses certain opinions with which one may not agree; nevertheless, teachers of a first course in soils will find that much of the "ABC of Soils" can be used as the XYZ of soils for students who are limited to one course in their curricula.

Louis T. Kardos

Bodenkunde für Landwirte, Forstwirte und Gärtner. Fifth Edition. By Eilhard Alfred Mitscherlich. Mas Niemeyer Verlag, Halle, Germany, 1949. PP. 364, figs. 43.

This is a fully revised edition of the author's book that first appeared in 1906. Its six chapters deal with physical, chemical, and plant physiological methods of investigating soils, plant-soil relationships, influence of climate on plant production, and practical applications. The appendix contains mathematical tables and formulas. The foreword includes the following impressive comment:

> I occupied myself with the writing of this book while a refugee, during which time I had come to the conclusion that the tragic war had destroyed the largest part of my own life's works. A majority of my best students are no longer alive and the greatest part of my numerous works are scarcely to be found. So, in a way, I give in the present book my scientific testament. May I be forgiven under these circumstances if I reassemble the greater part of my life's work.

George R. Blake

Chemical Activities of Fungi. By Jackson W. Foster. Academic Press, Inc., New York, 1949. Pp. 604. Price $9.50.

Fungi have been receiving increasing attention in recent years, primarily because of growing recognition of their importance in the decomposition of plant and animal residues; in the destruction of wood products, textiles, and other cellulosic materials; in the preparation of foodstuffs; in industrial fermentations; as causative agents of disease; and as producers of antibiotics. From the publication of Lafar's monumental "Handbuch der technische Mycologie" and of Czapek's "Biochemie der Pflanzen," more than three decades ago, until the appearance of Foster's book, no concentrated effort had been made, however, to systematize the information on the activities of this highly important group of microorganisms.

Foster's book is not a mere literature compilation. It presents the main outlines of the biochemistry of the fungi. The numerous facts are reinterpreted. The several chapters deal with: introduction, history, and perspective, methodology of mold metabolism, chemical nature of mold mycelium, general considerations of mold metabolism, natural variation, mutations, physiological genetics, and biochemical syntheses, trace element nutrition of fungi, lactic acid formation by fungi, alcoholic fermentation by molds, oxalic acid metabolism, fumaric and other C_4-dicarboxylic acids, citric acid, itaconic acid, kojic acid, gluconic and other sugar acids, carbohydrates produced by fungi, nitrogen metabolism of fungi, other transformations in fungi, and microbiological aspects of penicillin.

This reviewer would like more space devoted to enzymes of the fungi with extensive application in industry, such as the diastatic, proteolytic, and pectic enzymes, the numerous antibiotics produced by fungi, the effects of temperature, moisture, and other environmental factors upon the growth of fungi, the various aspects of spoilage and deterioration, and the mode of action of fungistatic and fungicidal agents. To treat these topics properly, however, would have required far more space than would be justified within the covers of a single book. The reader can be grateful to the author for having made this important contribution. All those who deal with fungi and their role in human economy will find this book indispensable.

SELMAN A. WAKSMAN

Annual Review of Biochemistry. Volume 18. Edited by J. MURRAY LUCK. Annual Reviews, Inc., Stanford, California, 1949. Pp. 739. Price $6.

This volume, like the preceding ones, should be of great interest and importance to all those who are concerned with research in plant and animal chemistry. The authors of its 23 chapters are men of prominence in their respective fields, and they bring a wealth of reading and research to bear in the presentation of their reviews. The subjects include biological oxidations; enzymes; chemistry of carbohydrates, lipids, amino acids, proteins, neoplastic tissue, hormones, and antibiotics; metabolism of lipids, amino acids, proteins, phosphorus compounds, carbohydrates, and fluorine and other trace elements; fat and water-soluble vitamins; nutrition of man; metabolic inhibitors; insect biochemistry; nitrogenous constituents of plants; organic acids in plants; and mineral nutrition of plants. Much of the material in the volume is of considerable interest to soil-plant scientists. Each presentation is followed by a long list of references. The work of some 5,000 specialists in these fields of research is reviewed.

Crisscross Trails. By MACY H. LAPHAM. Willis E. Berg, Berkeley, California, 1942. Pp. 246, figs. 32. Price $3.

The author of this book records the experiences of a lifetime in the service of the Soil Survey of the U. S. Department of Agriculture. Starting in September 1899, only 4 years after a Division of Agricultural Soils was created under the direction of Milton Whitney, the book continues through to the present organization under the direction of Charles E. Kellogg. A great many important persons in this field of work pass in review on its pages. Thus one makes the acquaintance of, or renews his acquaintance with, Geib, Briggs, Means, Gardner, Dorsey, Bonsteel, Mooney, Cameron, Fairchild, Scofield, Wiley, King, Coffey, Marbut, Bennett, Lapham, Rice, Mangum, Hunt, Shaw, Widtsoe, Hilgard, Hopkins, Knight, McCall, and many others. The book is full of reminiscences of a great variety of field experiences. The foreword was written by Kellogg. Men who have spent any considerable time in soil survey work will find the book expecially interesting. An index would have added materially to the reference value of the book.

Efficient Use of Fertilizers. Edited by VLADIMIR IGNATIEFF. Food and Agricultural Organization of the United Nations, Washington, D. C., 1949. Pp. 183, figs. 49. Price, paper bound, $2.

This is agricultural study No. 9, of a series of booklets being published by the FAO. The editor is to be congratulated on having pieced together in so effective a manner the statements prepared by the 36 contributors. The attractiveness of the publication is materially enhanced by some excellent photographs, notably those supplied by Charles E. Kellogg. The eight chapters are titled: the role of fertilizers; plant nutrients; the necessity for organic matter; commercial fertilizers and soil amendments; use of fertilizers, manures, and soil amendments; crop sequences and fertilizers; plant-nutrient relationships to soil regions; and the farmer and the agricultural services. Each chapter is followed by a list of references for further reading. A table of conversion factors for areas, weights, and measures is appended.

Energy Resources of the World. Department of State. Superintendent of Documents, Washington, D. C., 1949. Pp. 128, figs. 9. Price $2.25.

This report was brought together under the direction of Nathaniel B. Guyol as an aid in the formulation of the foreign policy of the United States. It contains a compilation of data on the occurrence, production, processing, trade, and utilization of energy resources. All resources of energy are expressed in terms of kilowatt-hours of electricity. The figures are on a triple-page scale and in color. The material in this report should be of great interest to many persons.

Handbook of Chemistry. Seventh Edition. Edited by NORTON ADOLPH LANGE. Handbook Publishers, Inc., Sandusky, Ohio, 1949. Pp. 1934. Price $7.

The author and his 75 capable collaborators have again rendered an exceptional service to scientists in general and to chemists in particular in the compilation of this book in its revised form. A considerable number of the tables have been extended or completely rewritten. The list of new tables include: abundance of the elements, glyceride content of drying oils, properties of hormones, ASTM classification of coals, formulas for calculating mineral-free BTU and fixed carbon, density of fuming sulfuric acid solutions, dielectric constants, dipole movements, mass of water in saturated air, partial pressures of aqueous ammonia solutions, Kopp's rule for calculating specific heat, logarithms of equilibrium constants, viscosity of aqueous sucrose solutions, and viscosity of aqueous ethyl alcohol solutions. Special attention is directed to the first-aid measures and to the table of common hazardous chemicals. This book fills a highly important need and will find almost daily use in every active chemical laboratory.

Hunger Signs in Crops. Second Edition. Prepared jointly by The American Society of Agronomy and the National Fertilizer Association. Judd and Detweiler, Inc., Washington, D. C., 1949. Pp. 390, figs. 118, color plates 124. Price $4.50.

The first edition of this book filled such an important need and was so well received that it became evident that a second edition should follow as soon as the material for it could be assembled. This edition covers much the same ground as the previous one, but in a more complete fashion. That rapid progress has been made in this field of research is quite evident in the new volume. The first chapter has to do with the general nutrient requirements of plants, and the remaining eight chapters deal with nutrient deficiencies in tobacco, corn and small grains, potatoes, cotton, vegetables, deciduous fruits, legumes, and citrus. The authors are men who have had special interest in the nutritional requirements of the crops assigned to them. They include Firman E. Bear, B. E. Brown, A. F. Camp, H. D. Chapman, H. P. Cooper, O. Wesley Davidson, Leroy Donald, G. N. Hoffer, G. V. C. Houghland, H. A. Jones, Wesley P. Judkins, B. A. Krantz, J. E. McNurtrey Jr., Werner L. Nelson, E. R. Parker, E. R. Purvis, George D. Scarseth, J. J. Skinner, and Norman J. Volk. The book is destined to enjoy very wide distribution, some 15,000 copies having been on order before it was published. All soil-plant scientists will want a copy close at hand for ready reference.

Introduction to Radiochemistry. By GERHART FRIEDLANDER AND JOSEPH W. KENNEDY. John Wiley and Sons, Inc., New York, 1949. Pp. 412. Price $5.

Both of the authors have had considerable experience in radiochemical research. The topics considered are: naturally occurring radioactive substances; atomic nuclei; nuclear reactions; sources of bombarding particles; quantitative treatment of radioactive processes; types of radioactive decay; interactions of radiations with matter; instruments; statistical considerations; the identification, concentration, and isolation of radioactive species; study of new elements; and tracers in chemical applications. A very valuable appendix contains tables of radioactive and stable isotopes, cross sections of isotopic thermal neutron activation, thick-target yields obtained with 14-Mev deuterons, and physical constants and conversion factors, and a selected list of 44 examination questions. Selected references are appended to each chapter. No previous knowledge of nuclear physics is required of the student. The authors are to be congratulated on having presented the subject in such a satisfactory manner. Those who have written books will appreciate the large amount of painstaking effort that went into the preparation of this volume.

Introduction to Soil Science. By G. W. LEEPER. Melbourne University Press, Victoria, Australia, 1948. Pp. 222, figs. 37, plates 12. Price 21s.

"The proper introduction to the study of the soil is not in the laboratory but in the field," according to the author of this book. Accordingly, the book begins with profiles and maps, soil types, and soil formation, then proceeds to a consideration of colloids, soil water, aeration, drainage, mechanical composition, and soil temperature, and, finally, deals with the chemistry of soils, with particular reference to plant needs. The appendix gives some suggestions for teachers' demonstrations, a selective bibliography of references, common and scientific names of plants, and a list of place names referred to in the text. The book is primarily designed for use in Australia. The author makes a special point of his intention to deal with the science rather than with the art of farming. The book merits special attention on the part of teachers who are searching for new ideas in instruction in this field of study.

Introductory Botany. By ALEXANDER NELSON. The Chronica Botanica Co., Waltham, Massachusetts, 1949. Pp. 479, figs. 121. Price $3.75.

This book provides a somewhat new approach to the teaching of botany. The author has endeavored to fit the presentation to the needs of the student who is interested in botany as a cultural subject and yet to have it meet the requirements of those who desire to prepare for more advanced studies in this field. The book is divided into three sections: the first, dealing with morphology, anatomy, and classification; the second, with gymnosperms and non-flowering plants; and the third, with physiology, plant distribution, and genetics. The discussion begins with some primary definitions and then proceeds with the general theme of adaptation and evolution. The illustrations, designed to supplement actual botanical specimens, are exceptionally well done and constitute a highly important part of the book. Anyone who masters the contents of this book will feel at home in any ordinary presentation dealing with plant science. Departments of botany might find it very much worth while to give this book a trial for classroom purposes. A second volume, dealing more particularly with the needs of students in medical schools, is in preparation.

Irrigated Soils, Their Fertility and Management. By D. W. THORNE AND H. B. PETERSON. The Blakiston Company, Philadelphia, 1949. Pp. 288, figs. 74. Price $5.

There has long been need for a good new text on the management of irrigated soils. This book meets that need admirably. Dedicated to Eugene Woldemar Hilgard and Franklin Stewart Harris, whose books on closely related subjects are agricultural classics, this book deals with the problems of irrigated arid regions; the nature of the soils; plant relationships; evaluating land for irrigation; application of water; drainage; reclamation of saline and alkaline soils; control of their physical, biological, and chemical properties; and soil management in relation to field crop, fruit, and vegetable production. A glossary and some useful tables of chemical information are appended. The material is lucidly presented, and the illustrations are excellent. The authors are to be congratulated on having done an excellent job of presenting important facts in relation to this type of agriculture.

The Journal of Soil Science. Volume 1, Number 1. Edited by G. V. JACKS. Oxford University Press, London, 1949. Pp. 122. Price per number 17/6.

This new journal is to be published annually. Two numbers constitute a volume. The first number contains 11 articles by well-known European soil scientists on the following subjects: effect of pH on electric charges carried on clay particles; climatic index for leaching factor in soil formation; frost soils on Mount Kenya and relation of frost soils to aeolian deposits; geomorphology and soil science; association of hydrologic sequence in certain soils of podzolic zone of northeast Scotland; podzolic soils of Wales; underwater soils: review of lake sediments; dependence of transpiration on weather and soil conditions; notes on recording and interpretation of x-ray diagrams of soil clays; x-ray defraction study of humification; and movement and precipitation of iron oxides in podzol soils. The quality of the papers in this first issue is of a high order.

Laboratory Manual and Problems in General Chemistry. By A. W. LAUBENGAYER. Rinehart and Company, Inc., New York, 1949. Pp. 230. Price $2.25.

This is a paper-bound manual for the use of beginning students in chemistry as well as those who have had some training in the subject. Blank spaces are provided for notes and blank pages for supplemental experiments and for recording solutions of the 336 problems contained in the manual. The appendix includes a series of tables of weights, measures, potentials, constants, solubilities, and other essential data, including the periodic table. The material is well prepared and should be very interesting to those who have to do with laboratory instruction, whether in chemistry or in other related sciences.

Make Friends with Your Land. By LEONARD WICKENDEN. The Devin-Adair Company, New York, 1949. Pp. 132. Price $2.50.

Another of the growing list of books dedicated to the development of "organiculture" as opposed to "chemiculture" of plants, this book repeats the arguments of Albert Howard and adds a few interesting touches. The possible quantity of compost that could be produced annually is set at 7,500 million tons and the cost of manufacturing it on a large scale at $1.35 a ton. Directions are given for producing compost. Special emphasis is given to Waksman's work with antibiotics as a possible explanation of the good effects of composts. The book merits reading, as do most of the others of this group, because there is a considerable element of truth as well as fancy in what is being written on this subject.

Man and His Physical Universe. Revised Edition. Edited by FRANK COVERT JEAN, EZRA CLARENCE HARRAH, AND FRED LOUIS HERMAN. Ginn and Company, 1949. Pp. 643. Price $4.

The purpose of this book is to present a course of instruction for nonscience students that cuts across the sciences to develop understandings "in such a way as to influence significantly the beliefs, philosophy, behavior, and attitudes of the future citizens of our democracy." With this in mind, science is considered under six headings: man's increased knowledge of the cosmos has modified his thinking; the fundamental distinction formerly supposed to exist between matter and energy has been broken down; matter as organized energy possesses properties which are indispensable to man; energy in many forms is used by man to advance civilization; the hydrosphere and the atmosphere are the chief factors of weather; and the earth's surface is continually changing. Each of these subjects is developed by reviewing the work of the more important scientists who have contributed to our understanding of it. A list of important references is appended to each of the 30 chapters. The book is well illustrated. It makes very interesting reading for the scientist, and it should be very useful for the purpose for which it is primarily intended.

The Nuffield Foundation Fourth Report. Secretary, LESLIE FARRER-BROWN. The University Press, Oxford, England, 1949. Pp. 127.

This is a report of a £10 million foundation established by Lord Nuffield 6 years ago. The general purpose of the foundation is to promote the health and well-being of mankind by assisting in the discovery of new knowledge in medicine and in the natural and social sciences. Large sums are being invested in basic scientific research and in the instruments that are necessary for its accomplishment in the United Kingdom. Fellowships and scholarships are being provided for study in other countries. Special interest is indicated in such problems as rheumatism and the care of aged poor. Eleven traveling scholarships have been awarded to young farmers to visit Canada, The United States, Scandinavian Countries, New Zealand, and Southern Rhodesia.

Le Phosphore et la Vie. By ALBERT DEMOLON AND ALBERT MARQUIS. Presses Universitaires de France, Paris, 1949. Pp. 118, figs. 9.

This paper-bound pocket edition deals with the distribution of phosphorus; its role in plant, animal, and human life; and its use in agriculture. Its tables show world consumption of mineral phosphates and of basic slag. This convenient-sized booklet is just what the graduate student, who is trying to develop a reading knowledge of French, needs to have in his pocket for reading practice during his spare moments of the day.

Plant and Soil Water Relationships. By PAUL J. KRAMER. McGraw-Hill Book Company, Inc., New York, 1949. Pp. 347, figs. 50. Price $4.50.

The approach to the subject of plant and soil water relationships is that of the plant physiologist. The book is designed to meet the need of plant scientists for an understanding of the principles involved. The discussion begins with a historical introduction, in which the early studies of Grew, Malpighi, Hales, De Candolle, and Dutrochet are reviewed. This is followed by chapters on soil-moisture relations, factors affecting the supply of soil moisture, its measurement and control, structure and growth of roots, factors affecting development of root systems, root and stem pressures and exudation phenomena, processes and factors affecting absorption of water and solutes, and absorption deficits and their effects on plants. An extended bibliography of some 700 important references is appended. The illustrations are excellent and well chosen to supplement the text. The method of presentation is that of a good teacher who endeavors to simplify the subject to the end that the various phenomena can be readily understood even by those who are not specialists in his field of study. The book merits an important place on the shelves of those who are concerned with plant production problems.

Principles of Field Crop Production. By JOHN H. MARTIN AND WARREN H. LEONARD. The Macmillan Company, New York, 1949. Pp. 1176, figs. 305. Price $6.

The authors are to be congratulated on having assembled such a wealth of very useful material on the principles of field crop production. The book is divided into five parts, of which the first deals with general principles, the second with crops of the grass family, the third with legumes, the fourth with miscellaneous crops, and the fifth, the appendix, with seeding rates, plant composition, conversion tables, and trade names of seed-treatment chemicals. The chapters on perennial forage grasses, miscellaneous legumes, and miscellaneous industrial crops are of special interest in that they introduce a considerable number of crop plants with which the average agronomist has had very little experience. A long list of important references is appended to each chapter. The illustrations are excellent. The appendix contains an extended glossary of agronomic terms. Both the common and the scientific names of plants are shown in the index. The book should gain an important place in agronomic literature.

The Principles of Soil Science. By ALEXIUS A. J. DE'SIGMOND. Thomas Murby and Company, London, 1949. Pp. 362, figs. 34. Price $5.50.

This appears to be a republication of the 1938 edition, which was translated by A. B. Yolland and edited by G. V. Jacks. The book is divided into four parts: genetics, agronomy, systematics, and cartography. The sections of Part II in the original that dealt with soil physics and soil microbiology have been omitted from this volume. The book, which should be of special value to pedologists, merits a place in every soils library. The author's definition of agronomy is of interest:

> The determination of types comes within the scope of agronomy, the branch of soil science which deals with the characterization of soils. The characteristics of soils may be divided into four groups—those revealed by field studies, and physical, chemical, and biological characteristics. Agronomy describes and systemizes the nature and pedological importance of these characteristics, and thus leads up to soil classification—or rather to

soil systematics. In the latter, the genetic basis is insufficient, indeed it is very often quite uncertain, particularly when dealing with soil horizons of non-typical formation.

Proceedings of the Inter-American Conference on Conservation of Renewable Natural Resources. The Department of State, Division of Publications, Office of Public Affairs, Washington, D. C., 1949. Pp. 782. May be obtained from the Superinintendent of Documents, Government Printing Office, Washington 25, D. C. Price $2.25.

This is publication 3382 of the Department of State. It covers the conference that was held at Denver, Colorado, September 7 to 20, 1948. The six sections deal with human populations and productivity capacity of the land, renewable resources and international relations, land use and the social sciences, dynamics of renewable resources, education in conservation dynamics, and making conservation effective. More than 100 papers were presented by specialists from essentially all of the Pan-American nations. The secretary-general was William Vogt. The papers are of such variety as to make difficult an adequate short review. Almost any scientist will find something of great interest to him in the papers presented. This is especially true for those who are concerned with the soil and plant sciences in relation to food production. Publication of a Spanish version of the proceedings is expected within the next year.

Quimica Coloidal del Suelo; I. Fenomenos de Superficie. By M. TSCHAPEK. Publications de Extension Cultural y Didactica, No. 3, Imprenta y Casa Editora (Coni), Buenos Aires, 1949. Pp. 344, figs. 118.

In this well-developed treatise on the colloidal chemistry of soils, the several chapters deal with edaphology, colloidal chemistry, adsorption, origin and properties of dispersed minerals, interaction of minerals and ions, Donnan equilibrium, and interaction of minerals, water, gases, and bacteria. Reference is made to the work of some 500 authors. The book is a highly constructive and well-demonstrated presentation and should be of much interest to soil physicists and physical chemists.

Radioactive Tracer Techniques. By GEORGE K. SCHWEITZER AND IRA B. WHITNEY. D. Van Nostrand Company, Inc., New York, 1949. Pp. 241, figs. 13. Price $3.25.

The purpose of this book is to serve as a guide for laboratory work in the use of radioactive tracers. The first part deals with the fundamentals, after which a series of basic, chemical, physical, and biological experiments are outlined. The remainder of the book deals with methods, peculiarities of radioactivity measurements, and properties of radioactive substances. Special attention is given to the hazards involved. One chapter deals with special preparations. The appendix includes an outline of a lecture course, form for writing up laboratory experiments, a statement on surgical gloves, radiolaboratory apparatus list, a list of suppliers, scales of 32 and 64, some radioisotopes of tracer interest, and a table of fundamental constants. The book fills a highly important place as an aid to instructional work in this field of study.

Streptomycin, Its Nature and Practical Applications. Edited by SELMAN A. WAKSMAN. The Williams & Wilkins Co., 1949. Pp. 618, figs. 95. Price $10.

The organism that produces streptomycin was first isolated in September 1943, at the New Jersey Agricultural Experiment Station. Now, 6 years later, we have this large volume that gives detailed records of the use of this antibiotic as a curative agent in a wide variety of human, animal, and plant ills, and a discussion of the problems related thereto. In the preface one reads: "Probably no other drug in the history of medical science has had such a phenomenonal rise as streptomycin." Later one notes that "in the presence of meningitis, the immediate results of the treatment may be dramatic." Again, an author reports that "streptomycin is already, by unanimous agreement, the most effective available agent in the treatment of tularemia." It is also shown that "streptomycin inhibits the growth of most of the gram-negative bacteria that are responsible for infection in the urinary tract." Finally, a plant pathologist concludes that "streptomycin may be useful in controlling seed-borne bacterial diseases of plants." The contributors number 58, including many well-known members of the university, medical, and industrial research staffs of the United States and Canada. The book covers the clinical uses, microbiological and chemical aspects, and the pharmacological properties of the product, and amply justifies its existence for that purpose alone. But it is entitled to a much wider reading by those who desire or need to know something more definite about the possibilities of the scientific method when rigidly applied to the solution of pressing problems.

Studies in Plant Life. Second Edition. By HARVEY E. STORK. Burgess Publishing Co., Minneapolis, Minnesota. Pp. 115. Price $3.

This is a loose-leaf laboratory guide, bound in cardboard and with a coiled-wire back. It covers one semester's work in 16 units. These include gross structure, the cell, kinds of cells and tissues, typical leaf structure, atypical leaf, chlorophyll and photosynthesis, light and gas relations, respiration, roots, transpiration, endogenous stem, exogenous stem, wood, flower, fruit, and heredity. Excellent illustrations are shown, and blank space is available for students' notes and drawings. Each chapter is concluded with a selected bibliography. A list and key to common species of trees are shown. A 9-page glossary is appended. The manual is intended to aid the student "to see clearly and understand thoroughly the plant or plant parts studied each day." The material is exceptionally well designed for the purposes in mind.

THE EDITORS

BEHAVIOR OF HYDROGEN IN ION-EXCHANGE REACTIONS[1]

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In recent studies of the properties of a number of ion-exchange materials (2, 3,) very satisfactory expressions were developed for the exchange between a large number of ion pairs. These expressions have been found appropriate for monovalent, divalent, and trivalent ions over wide variations in ion concentration and in amount of adsorbent.

A notable exception, however, was encountered in ion pairs involving hydrogen. It was found that the equilibrium conditions for exchange processes with hydrogen cannot be predicted by means of any theory proposed thus far. This is the case with a variety of adsorbents such as clays, soil colloids, and synthetic resins.

The anomalous behavior of H^+ in the exchange reactions of soil colloids was noted a good many years ago by Jenny (4). The phenomenon seems to have missed the attention of scientists in other fields. Even as late as 1947, Boyd *et al.* (1) in reporting their work on synthetic resins implied that H ion can be treated by methods applicable to other ions.

A possible reason for the H problem may be found in the fundamental assumptions necessary for formulation of any ion-exchange equation. In a recent treatment of the theory of ion-exchange (2), the authors pointed out that since exchange equations contain concentrations of ions only, certain assumptions are implicit in all equations of this kind. Most important of these is the assumption that either the specific interaction energies of the ions in question with the charged surface and with the molecules of the medium are constant over a wide variety of conditions or their differences for a chosen pair of ions is constant. Unless this condition is fulfilled no ion-exchange formulation based on concentration terms is possible.

For pairs of ions that are completely "dissociated," that is, ions which interact with the surface by purely electrostatic forces of ordinary strength, this assumption appears reasonable. On the other hand, for ions that may be held to the surface by covalent bonds or the unusually strong electrostatic bonds of very small ions as well as by ordinary electrostatic forces, it seems that their specific interactions or the difference between their interactions and those of other ions would not be independent of their amounts. This might very well be the case with hydrogen ion, since considerable evidence points to the fact that adsorbed hydrogen in clays and soil colloids is not completely "dissociated."

Thus a rigorous treatment of the hydrogen problem would seem to require calculation of a "dissociation constant" for adsorbed hydrogen. The determination of such a constant must be indirect, since the "dissociation" occurs entirely within the adsorbent phase. This problem will be considered in a later paper.

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[1] Taken from a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of doctor of philosophy in soil chemistry, 1949.

On the other hand, because hydrogen appears to be unique among ions in its behavior, certain solutions of the hydrogen problem by the arbitrary use of convenient parameters are possible. These solutions are particularly worthwhile, because of their simplicity and usefulness. One such treatment of the problem follows.

SOLUTION OF THE HYDROGEN PROBLEM BY USE OF PARAMETERS

In many exchange studies (3), it has been found that the formulation based on the theory of Guggenheim gives a very satisfactory exchange constant between any chosen ion pair not involving H^+. This was found to be true regardless of the amounts of other ionic species in the system, including hydrogen. Numerous experiments with clays and synthetic resins have been made in which the amounts of H(*ad*) remaining on the adsorbent varied from about 10 per cent to 90 per cent. Even with such a wide variation, the exchange constants for the pairs NH_4–K, Rb–Ca, and Cs–La on clays and NH_4-K, K–Ca, Rb–Ca, Cs–La, and Rb–La on the resin IR 100 were the same as those obtained with systems containing only the pair of ions under consideration. On the basis of these experiments the following argument seems valid: If none of the complementary ions including H(*ad*) has an effect on the exchange constant between any other pair of ions, then it is reasonable to conclude that any given complementary ion will have no effect on the distribution of H between the adsorbent and the aqueous phase in comparison with a similar distribution of any other ion. This conclusion provides a basis for the solution of the hydrogen problem.

With this argument in mind, let us consider an equilibrium system consisting of an adsorbent phase and an aqueous phase and containing a number of ionic components such as Na, K, H, Ca, and La. Now, as the amounts of the ionic components are varied over wide limits, it has been experimentally demonstrated that the following ionic exchange expressions based on a modification of Guggenheim's theory are correct:

$$\frac{\mathrm{K}(ad)}{(\mathrm{K}^+)} \cdot \frac{(\mathrm{Na}^+)}{\mathrm{Na}(ad)} = k_{\mathrm{K-Na}} \tag{1}$$

$$\frac{\mathrm{K}(ad)^2}{(\mathrm{K}^+)^2} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}(ad) \cdot \mu} = k_{\mathrm{K-Ca}} \tag{2}$$

$$\frac{\mathrm{K}(ad)^3}{(\mathrm{K}^+)^3} \cdot \frac{(\mathrm{La}^{+++})}{\mathrm{La}(ad) \cdot \mu^2} = k_{\mathrm{K-La}} \tag{3}$$

where the quantities in parentheses denote activities of the ions in the aqueous phases and $\mu = \Sigma q_i C_i = [2\ \mathrm{La}(ad) + 1\frac{1}{2}\ \mathrm{Ca}(ad) + \mathrm{K}(ad) + \mathrm{Na}(ad) + \mathrm{H}(ad) + \ldots]$.

Similar expressions can be shown to be valid for all ion pairs except those involving H^+. That is, we find experimentally:

$$\frac{\mathrm{H}(ad)}{(\mathrm{H}^+)} \cdot \frac{(\mathrm{K}^+)}{\mathrm{K}(ad)} \neq \text{constant} \tag{4}$$

$$\frac{\mathrm{H}(ad)^2}{(\mathrm{H}^+)^2} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}(ad)\cdot\mu} \neq \text{constant} \tag{5}$$

$$\frac{\mathrm{H}(ad)^3}{(\mathrm{H}^+)^3} \cdot \frac{(\mathrm{La}^{+++})}{\mathrm{La}(ad)\cdot\mu^2} \neq \text{constant} \tag{6}$$

As a possible solution to this problem, let us assume that for the foregoing systems an unknown function, $f\mathrm{H}(ad)$, of the adsorbed hydrogen exists such that for a particular value of $\frac{\mathrm{H}(ad)}{\mu}$:

$$\frac{a_{\mathrm{H}(ad)}}{a_{\mathrm{K}(ad)}} = \frac{f\mathrm{H}(ad)}{\mu} \bigg/ \frac{\mathrm{K}(ad)}{\mu} = \frac{f\mathrm{H}(ad)}{\mathrm{K}(ad)}$$

$$\frac{a^2_{\mathrm{H}(ad)}}{a_{\mathrm{Ca}(ad)}} = \frac{[f\mathrm{H}(ad)]^2}{\mu^2} \bigg/ \frac{\mathrm{Ca}(ad)}{\mu} = \frac{[f\mathrm{H}(ad)]^2}{\mathrm{Ca}(ad)\cdot\mu}$$

$$\frac{a^3_{\mathrm{H}(ad)}}{a_{\mathrm{La}(ad)}} = \frac{[f\mathrm{H}(ad)]^3}{\mu^3} \bigg/ \frac{\mathrm{La}(ad)}{\mu} = \frac{[f\mathrm{H}(ad)]^3}{\mathrm{La}(ad)\cdot\mu^2}$$

where $a_{H(ad)}$ etc. refer to ionic activities. Then

$$\frac{f\mathrm{H}(ad)}{(\mathrm{H}^+)} \cdot \frac{(\mathrm{K}^+)}{\mathrm{K}(ad)} = k_{\mathrm{H-K}} \tag{7}$$

$$\frac{[f\mathrm{H}(ad)]^2}{(\mathrm{H}^+)^3} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}(ad)\cdot\mu} = k_{\mathrm{H-Ca}} \tag{8}$$

$$\frac{[f\mathrm{H}(ad)]^3}{(\mathrm{H}^+)^3} \cdot \frac{(\mathrm{La}^{+++})}{\mathrm{La}(ad)\cdot\mu^2} = k_{\mathrm{H-La}} \tag{9}$$

Although the existence of such a function $f\mathrm{H}(ad)$ seems highly probable for a large number of systems, it is not subject to direct estimation. On the other hand, $f\mathrm{H}(ad)$ can be arbitrarily defined by means of the expression

$$f\mathrm{H}(ad) = \frac{\mathrm{K}(ad)}{(\mathrm{K}^+)} \cdot (\mathrm{H}^+) \tag{10}$$

Then by substitution of the value of $f\mathrm{H}(ad)$ so defined in equations *(7)*, *(8)*, and *(9)*, the exchange constants $k_{\mathrm{H-K}}$, $k_{\mathrm{H-Ca}}$, and $k_{\mathrm{H-La}}$ assume the arbitrary values of 1, $k'_{\mathrm{H-Ca}}$, and $k'_{\mathrm{H-La}}$.

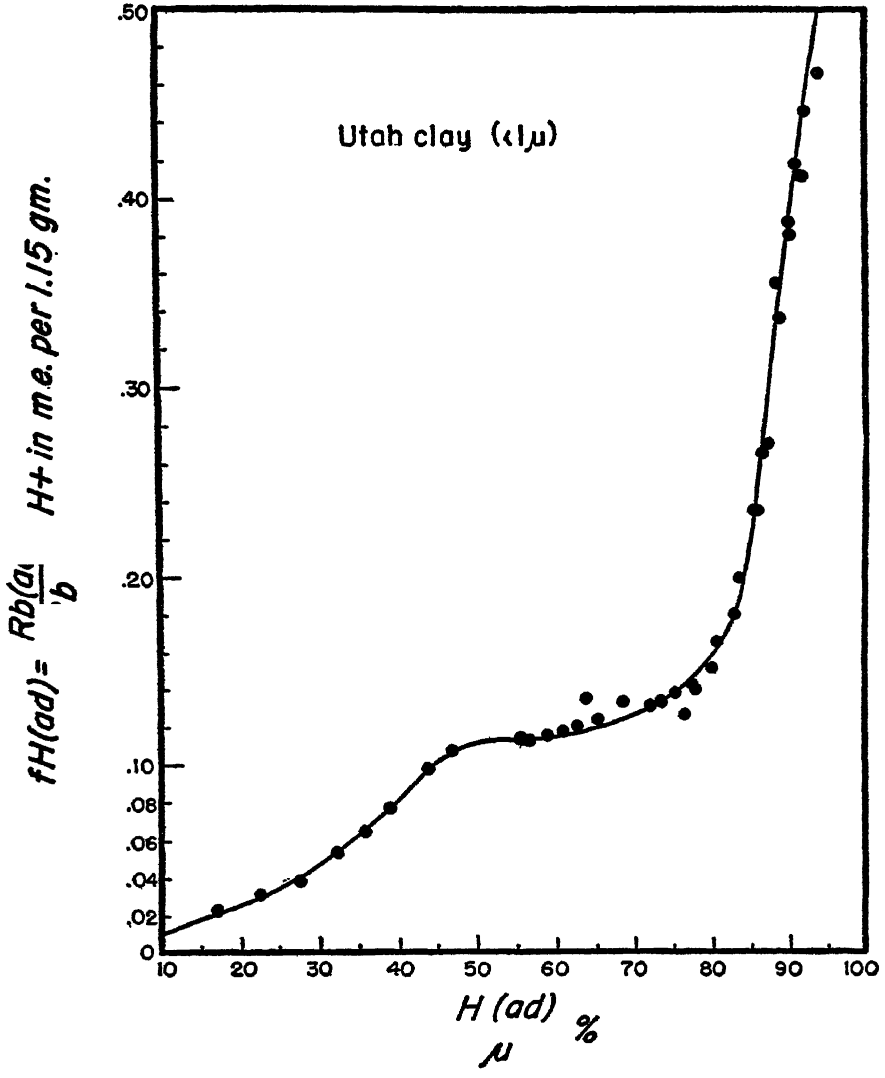

Fig. 1. Relation of $fH(ad)$ to $\frac{H(ad)}{\mu}$ for Utah Bentonite

Justification for the foregoing procedure can be tested experimentally by calculating $fH(ad)$ by means of equation (*10*) for a wide range of values of $\frac{H(ad)}{\mu}$ and observing the constancy of k'_{H-Ca}, k'_{H-La}, etc.

It is immaterial whether $fH(ad)$ is defined with respect to K, Na, Rb, Ca, or La, because the equilibrium constant between any pair of these ions is unaffected by the amount of H(*ad*) and other complementary ions. Thus $fH(ad)$ defined above as $\frac{K(ad)}{(K^+)} \cdot (H^+)$ will differ from $fH(ad)$ defined with respect to Rb or Ca by con-

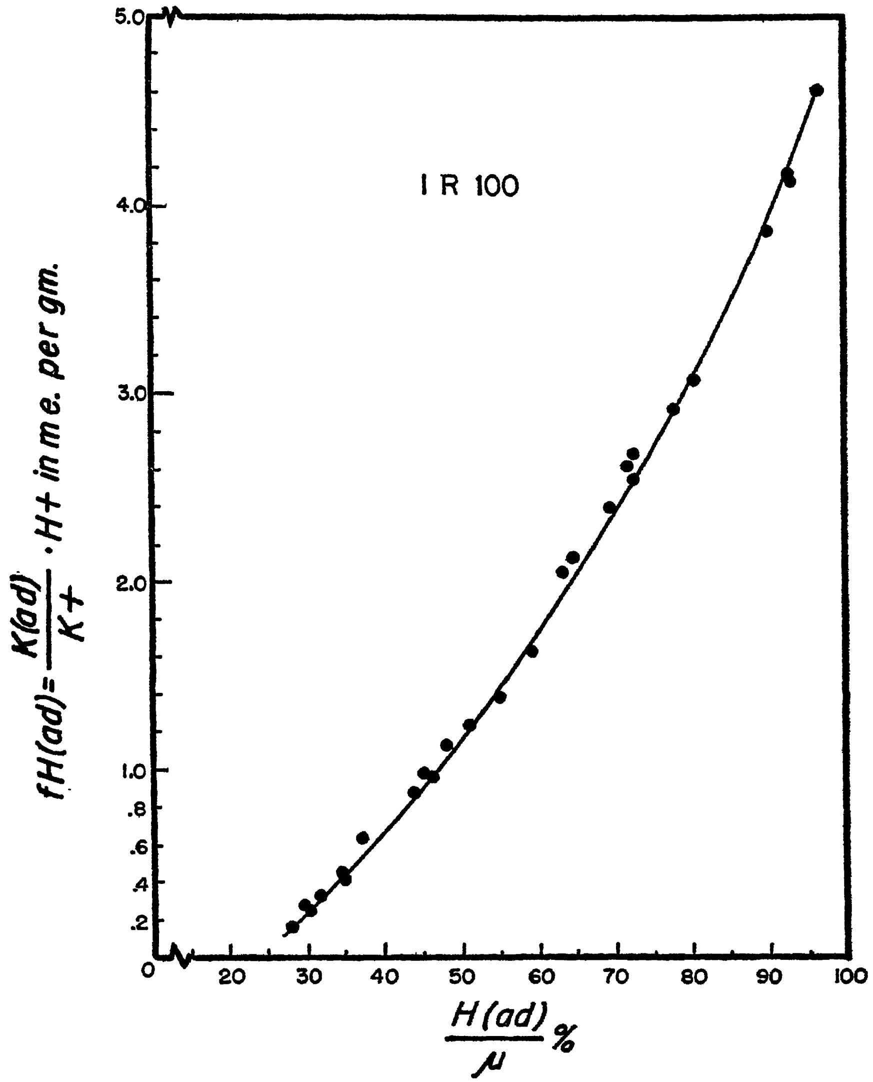

FIG. 2. RELATION OF $f\mathrm{H}(ad)$ TO $\frac{\mathrm{H}(ad)}{\mu}$ FOR THE SYNTHETIC RESIN IR 100

stant factors. These factors are equal to the exchange constants between Rb and K or Ca and K.

EXPERIMENTAL DETERMINATION OF $f\mathrm{H}(ad)$

For the region of high values of $\frac{\mathrm{H}(ad)}{\mu}$, a known amount of H-adsorbent was equilibrated with varying amounts of KCl in a constant volume. The amounts of K^+ and H^+ were then determined and K(*ad*) and H(*ad*) were estimated by difference. Then $f\mathrm{H}(ad)$ was calculated by means of equation (*10*). For the middle values of $\frac{\mathrm{H}(ad)}{\mu}$ it was often found preferable to carry out the experiments with RbCl or CsCl instead of KCl. The values of $f\mathrm{H}(ad)$ so obtained were then converted to the same basis by multiplying by appropriate known exchange constants. For the region of low values of $\frac{\mathrm{H}(ad)}{\mu}$, K-adsorbents, Rb-adsorbents, or Cs-adsorbents were equilibrated with HCl, and $f\mathrm{H}(ad)$ was determined as previously.

TABLE 1

Equilibrium data for the H-Cs exchange on Utah bentonite

1.15 gm. clay = 1.498 me. was used in all cases. All concentrations are given in terms of me. per 100 ml. of suspension

$\mathrm{H}(ad)$	H^+	$\mathrm{Cs}\,(ad)$	Cs^+	$\frac{\mathrm{H}(ad)}{\mathrm{H}(ad)+\mathrm{Cs}(ad)}$	$f\mathrm{H}(ad) = \frac{\mathrm{Rb}(ad)}{(\mathrm{Rb}^+)} \cdot (\mathrm{H}^+)$ graphic	$k = \frac{\mathrm{H}(ad)}{(\mathrm{H}^+)} \cdot \frac{(\mathrm{Cs}^+)}{\mathrm{Cs}(ad)}$	$k' = \frac{f\mathrm{H}(ad)}{(\mathrm{H}^+)} \cdot \frac{(\mathrm{Cs}^+)}{\mathrm{Cs}(ad)}$
				per cent			
1.431	2.155	.067	.057	95.5	.576	0.565	.227
1.322	1.727	.176	.196	88.3	.356	0.853	.230
1.208	0.834	.290	.330	80.7	.166	1.648	.221
1.075	0.612	.423	.445	71.8	.132	1.832	.227
0.960	0.538	.558	.558	62.8	.122	1.786	.222

TABLE 2

Equilibrium data for the H–Ca exchange on resin IR 100

1.0 gm. resin = 1.72 me. was used in all cases. All concentrations are given in terms of me. per 100 ml. of suspension

$\mathrm{H}(ad)$	H^+	Ca^{++}	$\mathrm{Ca}(ad)$	$f\mathrm{H}(ad) = \frac{\mathrm{K}(ad)}{(\mathrm{K}^+)} \cdot (\mathrm{H}^+)$ graphic	$k = \frac{\mathrm{H}(ad)^2}{(\mathrm{H}^+)^2} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}(ad)[1\tfrac{1}{2}\mathrm{Ca}(ad)+\mathrm{H}(ad)]}$	$k' = \frac{f\mathrm{H}(ad)^2}{(\mathrm{H}^+)^2} \cdot \frac{(\mathrm{Ca}^{++})}{\mathrm{Ca}(ad)[1\tfrac{1}{2}\mathrm{Ca}(ad)+\mathrm{H}(ad)]}$
1.219	5.721	.0293	0.501	2.83	1.08×10^{-3}	5.78×10^{-3}
1.128	5.812	.0439	0.592	2.50	1.17×10^{-3}	5.64×10^{-3}
0.967	5.973	.0948	0.753	1.96	1.39×10^{-3}	5.72×10^{-3}
0.737	3.071	.0767	0.983	1.18	2.10×10^{-3}	5.42×10^{-3}
0.486	2.278	.356	1.234	0.44	6.78×10^{-3}	5.71×10^{-3}

The values of $f\mathrm{H}(ad)$ for Utah bentonite calculated with respect to Rb, $f\mathrm{H}(ad) = \frac{\mathrm{Rb}(ad)}{(\mathrm{Rb}^+)} \cdot (\mathrm{H}^+)$, are plotted against $\frac{\mathrm{H}(ad)}{\mu}$ in figure 1. For the resin, IR 100, $f\mathrm{H}(ad)$ calculated with respect to K is plotted against $\frac{\mathrm{H}(ad)}{\mu}$ in figure 2. It will be noted from the graphs that $f\mathrm{H}(ad)$ has the units of milliequivalents per unit weight.[2]

[2] When used in an exchange equation $f\mathrm{H}(ad)$ must have the units of milliequivalents per unit volume. When the concentration of adsorbent is known, however, the values of the table can be readily expressed in these terms also.

USE OF GRAPHS OF $f\mathrm{H}(ad)$

Having plotted $f\mathrm{H}(ad)$ against $\frac{\mathrm{H}(ad)}{\mu}$ for a given adsorbent, one can, theoretically, calculate, by means of the graph and equilibrium data, a satisfactory exchange constant for any ion pair involving hydrogen. For example, the values of $f\mathrm{H}(ad)$, calculated with respect to Rb, for Utah bentonite are obtainable from figure 1. Equilibrium data for the H–Cs exchange in Utah bentonite are given in table 1. The values of the exchange constant calculated in terms of H(*ad*) and $f\mathrm{H}(ad)$ are given in the last two columns of the table.

Similarly, from data for the H–Ca exchange on the resin IR 100, values of the exchange constant calculated from H(*ad*) and $f\mathrm{H}(ad)$ (from figure 2) are presented in the last two columns of table 2.

DISCUSSION AND SUMMARY

Experimental data such as those reported in tables 1 and 2 indicate that the arbitrarily defined and experimentally determined function $f\mathrm{H}(ad)$ can be used successfully for calculation of ion-exchange constants for ion pairs involving hydrogen. That is, once a graph of $f\mathrm{H}(ad)$ versus $\frac{\mathrm{H}(ad)}{\mu}$ has been constructed for a given material, the problem of formulation of satisfactory expressions for exchanges with hydrogen in the material is practically solved.

The function $f\mathrm{H}(ad)$ as defined is uniquely determined by the value of $\frac{\mathrm{H}(ad)}{\mu}$ as long as one works with a constant amount of the adsorbent. It should be noted, however, that although $\frac{\mathrm{H}(ad)}{\mu}$ is dimensionless, $f\mathrm{H}(ad)$ as defined has the dimensions of concentration and is conveniently expressed in terms of milliequivalents per gram of adsorbent. It will vary linearly, therefore, with the amount of adsorbent used for experimentation. In the calculation of equilibrium constants this fact must be taken into consideration.

It is to be noted that $f\mathrm{H}(ad)$ defined as above is very different from the pH of the suspension. For example, $f\mathrm{H}(ad)$ is independent of particle size and the kind of complementary ions. The pH of a suspension is strongly influenced by these factors. Moreover, it is well known that the pH does not vary linearly with the amount of adsorbent.

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A SIMPLE VOLUME-WEIGHT SAMPLER AND PROCEDURE

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Measurements of the apparent specific gravity or volume weight of soils are useful in determining porosity as an index of soil structure. They also have important practical applications for the conversion of soil water from a weight to a volume basis. Expressing soil moisture in inches-depth of water per foot of soil simplifies the analysis and discussion of what happens to precipitation or irrigation water after it enters the soil profile.

Several methods (4, 9, 11, 12) have been proposed for measuring volume weight. Use of a soil tube to remove a core of soil in its natural structure is now common because of its ease of sampling. Numerous types and sizes of soil-sampling tubes have been used by soil investigators, engineers, and agronomists (2, 3, 5, 6, 7, 8, 10, 11, 12). Very little information is available on the instrumental error and reliability of these instruments. It is believed that tubes of small diameter cause compression and that hammering the cylinder results in shattering the soil. A sampler that eliminates these objectionable alterations of the soil should give a reliable measure of pore volumes.

DESCRIPTION OF SAMPLER

A volume-weight sampler and procedure were developed and used on the Guayule Emergency Rubber Project[2]. This sampler was used in studies of certain agricultural soils in California and Texas. More recently it has been used in studies of the relationship between soil structure and infiltration capacity on mountain range land in Colorado. One of the aims of the latter studies was to determine the effect of trampling by livestock on soil compaction and how this reduction in noncapillary porosity affects infiltration capacity of the soil. The sampling equipment and procedure have given satisfactory results, both on the mountainous timber and range lands and on agricultural alluvial soils.

The sampling equipment is shown in figures 1 and 2. It consists mainly of three sampling tubes, tube plug, hydraulic jack, and extraction bracket[3]. A small metal pan and oilcloth, or tarpaulin, can be used for collecting any soil spilled during the cutting and extraction process. The equipment is constructed of seamless steel tubing of various gages, boiler plate steel, and strap iron. Tubing of standard size may have to be turned down on a lathe to obtain the indicated dimensions. A maximum 3-inch length of soil core is obtainable with the tube shown, but the equipment may be modified accordingly for any length needed. Also, a tube-diameter of $4\frac{13}{32}$ inches provides a simple conversion factor of 250 cc. of volume per inch of core length.

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[1] Maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with Colorado A & M College at Fort Collins, Colorado.

[2] Dortignac, E. J. Guayule response to soil moisture under dryland culture in California (Processed). Emergency Rubber Project Report. 1946.

[3] The equipment shown is heavier than needed for most sampling conditions. Where sampling locations can be reached only on foot, the equipment can be lightened by employing a smaller hydraulic jack and duralumin material.

In Guayule Emergency Rubber Project investigations by the writer during 1942 and 1943, soil cores were taken with tubes that varied in size from $\frac{7}{8}$ inch (11) to about 3.5 inches. Although the smaller tube allowed sampling of the deeper soil layers, it was discarded for volume-weight determinations because of the large sampling error. Variable compression of the soil contributed a large part of the error. When soil cores measured less than the amount sampled, it was sometimes difficult to determine whether gravel forced ahead of the tube or compression of soil was responsible for the shortened core length. Inserting a calibrated rod into the tube before and after its extraction from the soil made it possible to ascertain whether any soil was lost while the tube was being pulled out. Length of soil core was also checked by measurements after removal from the tube.

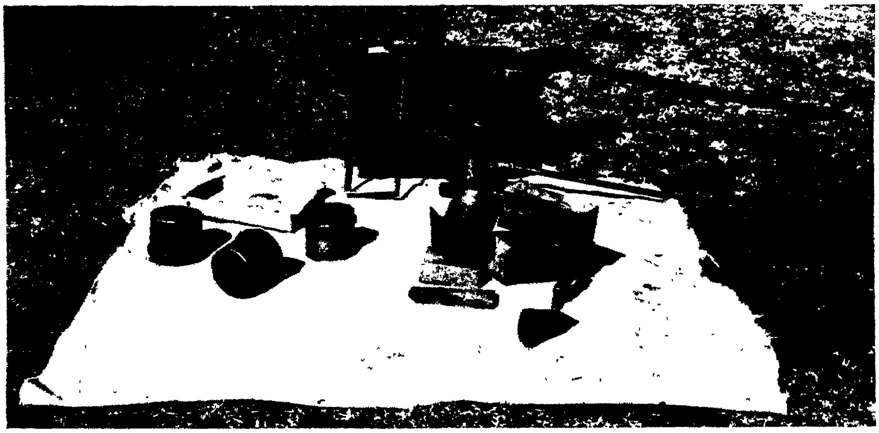

FIG. 1. VIEW OF SAMPLING EQUIPMENT WITH WOODEN STORAGE BOX

Some idea of discrepancy between volume weights obtained with variable sized tubes as well as sampling variations are presented in table 1. Samples represent averages for two sites on Ramona sandy loam near March Field in southern California. Soil profiles were very similar at these two locations, though variations in soil contributed somewhat to sampling error. The mean values and deviations represent about 20 samples at each depth with the small tube and only a few replications with the larger tubes. Even so, the sampling error of the larger tubes was much smaller. Variation between replications decreased with each successive increase in tube diameter. Volume weights obtained with the smaller tube are given both on the basis of actual soil-core length and that determined by outside measurements on the tube before and after it was driven into the soil. Only soil cores measuring more than 80 per cent of the length indicated by markings on the outside of the $\frac{7}{8}$-inch tube were used in this comparison.

Samples were taken at the wilting point and at the field capacity. Moisture content ranged from 4.6 to 5.8 per cent at wilting point and from 10.0 to 11.7 per cent at field capacity. Upper limits represent the B horizon and lower limits the surface foot of the A horizon. Apparently moisture content had little effect on volume weight in this soil type.

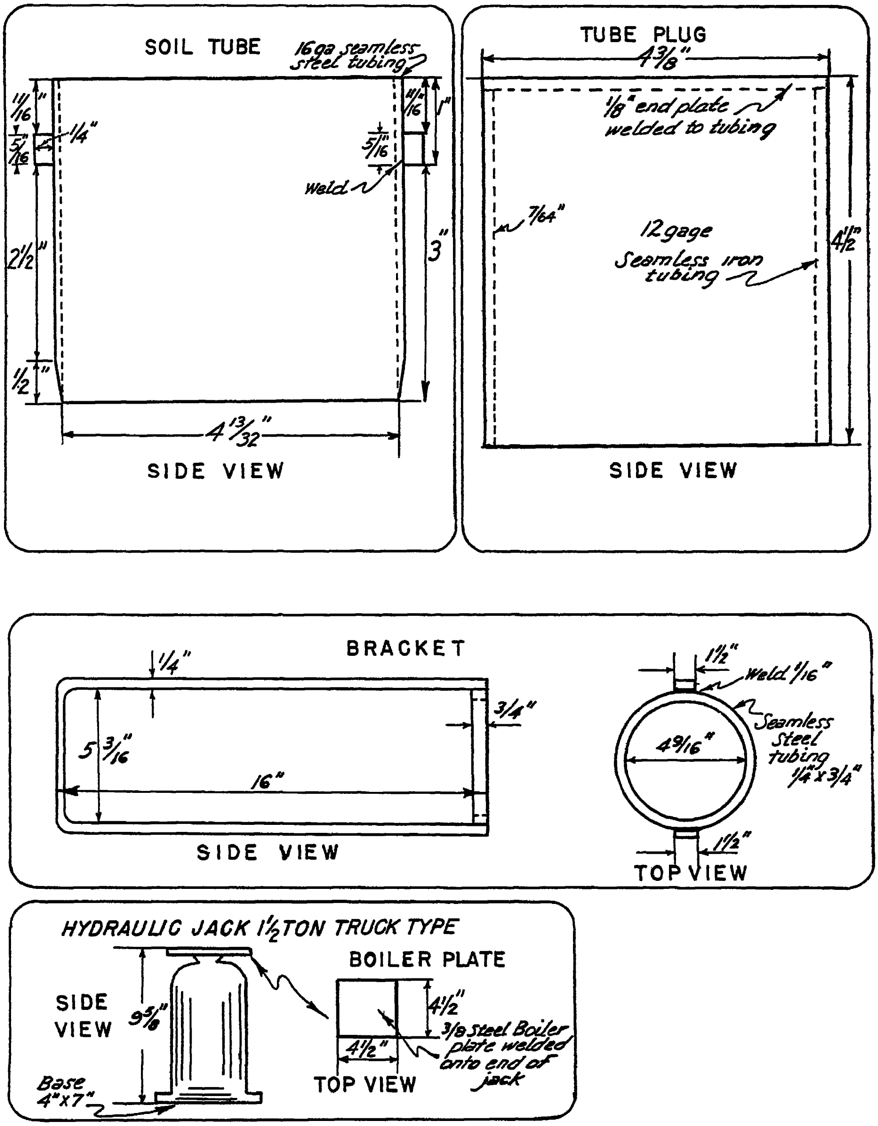

FIG. 2. VOLUME-WEIGHT SAMPLER

Volume weight determined by outside measurements on the small diameter tube corresponded more closely to values obtained with the larger tubes at both moisture contents. Yet, no significant regression could be established between volume weights obtained with these tubes. Correlations were even poorer in several other soil types studied, and relationships were not consistent from soil to soil.

FIELD PROCEDURE

Samples may be taken at any moisture content, but those taken at the field capacity furnish one of the most accurate measures of the true capillary porosity of the soil. Also, the sampling procedure is improved, since the soil core does not break up so readily as when dry. This is desirable in very coarse soils, particularly when the sample may be taken to the laboratory for permeability or other physical measurements requiring an intact core.

TABLE 1

Comparison of mean volume weights and deviations determined at wilting point and at field capacity with variable sized tubes

Ramona sandy loam—near March Field, Calif.

HORIZON	SOIL DEPTH ft.	TEXTURE*	SAMPLES AT WILTING POINT			SAMPLES AT FIELD CAPACITY		
			⅞-inch tube		3⅝-inch tube	⅞-inch tube		1⅞-inch tube
			Measured core	Tube meas.		Measured core	Tube meas.	
			Volume weight					
A	0–1	Sandy loam	1.69	1.33	1.45	1.65	1.56	1.48
A	1–2	Sandy loam	1.71	1.49	1.53	1.53	1.45	1.50
B	2–3	Loam	1.62	1.52	1.60	1.75	1.64	1.63
C	3–4	Sandy loam	1.62	1.52	1.50	1.49	1.41	1.53
C	4–5	Sandy loam	1.60	1.53	1.46	1.57	1.49	1.38
			Standard deviation ±					
A	0–1	Sandy loam	0.33	0.23	0.07	0.27	0.17	0.09
A	1–2	Sandy loam	0.23	0.15	0.04	0.08	0.11	0.10
B	2–3	Loam	0.11	0.09	0.03	0.17	0.28	0.08
C	3–4	Sandy loam	0.16	0.22	0.03	0.16	0.10	0.06
C	4–5	Sandy loam	0.22	0.20	0.04	0.24	0.32	0.10

* Soil textures in this and subsequent tables based on the Bouyoucos method for mechanical analysis (1).

In the guayule-soils investigations a rectangular pit about 3 by 8 feet and 6 to 7 feet deep was dug. Samples were obtained by horizon and textual changes. The soil cores were taken from one face of the excavation by impressing a 3⅝-inch[4] tube from 4 to 6 inches (indicated by markings on the outside of cylinder) laterally into the earth (pit wall) by means of the hydraulic jack (fig. 3). Slow steady strokes were found superior to rapid motion in reducing the amount of compression.

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[4] This diameter core fits in the standard 16-ounce friction sampling can.

After the cylinder was forced into the soil to the required depth, the tube plug was inserted in the open end of the cylinder to prevent any loss of soil sample or entrance of any extraneous material into the tube during the excavation.

The tube was removed by carefully digging away the surrounding soil. The soil core was next smoothed off even with the cylinder by means of a sharpened trowel or hacksaw with the set ground off the teeth. This procedure tends to smear or seal the pores, particularly in fine-textured soils. This action may interfere with laboratory permeability or suction-table tests and is an important reason for favoring field determination of capillary porosity.

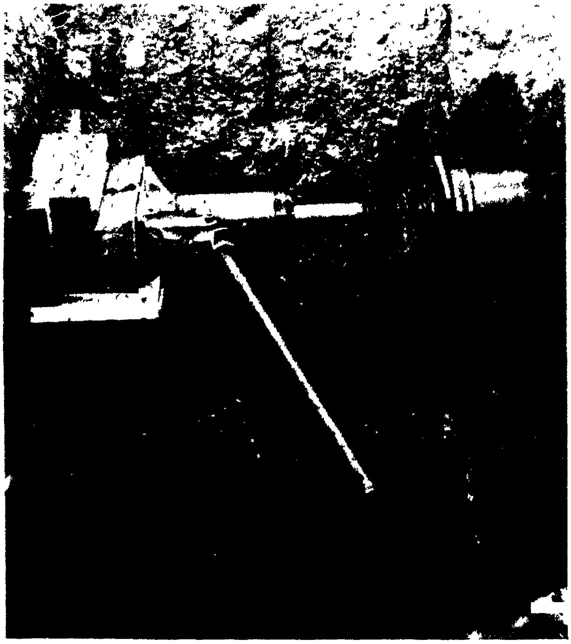

Fig. 3. Soil Cylinder Forced Laterally into the Side Wall of an Excavated Pit—Uvalde Silty Clay Loam, San Antonio, Texas

The soil core was extracted from the sampling tube by use of the hydraulic jack, tube plug, and special bracket. The length of soil core was measured and checked against that indicated by markings on the outside of the tube. The maximum amount of compression experienced with the 3⅝-inch diameter tube in a 4-inch core length was 0.15 inch. This value was obtained in the surface soil of Lewisville silty clay near Seguin, Texas. The average compression in 20 soils ranging from loamy sand to clay in both California and Texas amounted to about 2 per cent. Compression varied both with moisture and with soil type. Very little compression occurred in samples taken in coarse-textured soils.

The procedure employed in measuring soil structure as related to infiltration capacity on the mountain range lands was modified because of the different requirements. It was felt that the capillary and noncapillary porosity and volume weight of the soil nearest the surface would be more closely associated with its infiltration capacity. Therefore, cores of each of the top 3 inches of soil were taken in every infiltration plot several days[5] after completion of the run, allowing the soil sufficient time to drain to the field capacity.

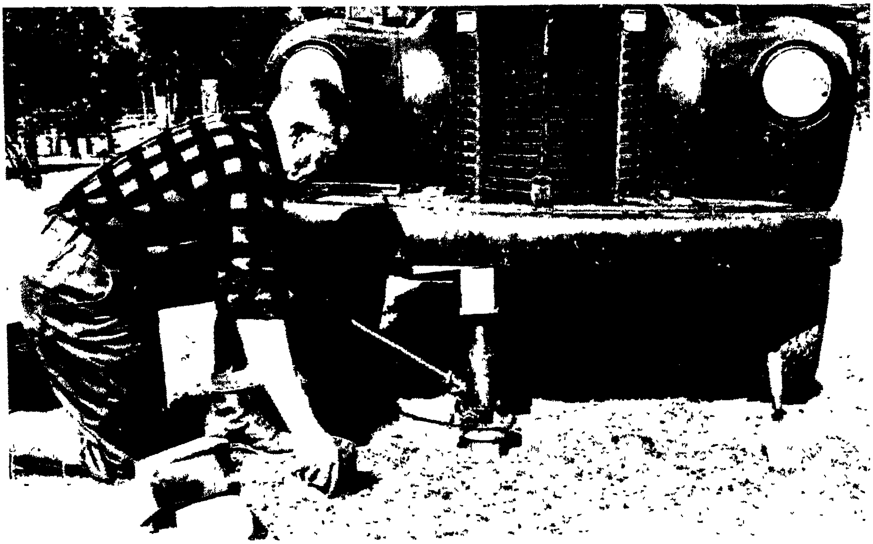

FIG. 4. EMPLOYING THE FRONT BUMPER OF A 1½-TON TRUCK FOR FORCING THE CYLINDER INTO THE SOIL—MANITOU EXPERIMENTAL FOREST, COLORADO

The front bumper of a 1½-ton truck was used for forcing the $4\frac{13}{32}$-inch tube into the soil by means of the hydraulic jack (fig. 4). The truck was used at each of the 54 plot locations, including the timbered as well as grassland areas on slopes varying from 2 to 30 per cent.[6] Pressure was applied slowly and steadily so as to avoid compressing the soil. Numerous comparisons of measurements of the soil-surface

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[5] Approximately 3 to 5 days were allowed for internal drainage, depending on the texture. Since plot surfaces were adequately covered with tarpaulins and plot frames had cut vegetative roots to a 3-inch depth, evaporation and transpiration losses were minimized during the drainage period.

[6] The truck is part of the infiltrometer equipment and was used for jacking in the tube. Another method that may be employed is to sink two screw-type soil augers into the ground about 5 feet apart and attach a steel cross-member to the auger handles.

level within and outside the tube and of the soil-core length before, during, and after extraction from the tube showed no measurable compression. Certain investigators (10, 12) have recommended lubricating the soil cylinder with petroleum jelly or mercury both inside and outside before forcing it into the soil. Lubrication is not necessary with this sampling equipment when the large diameter tube is used. After the tube was forced into the soil to a 3-inch depth, the plug was inserted, and then the tube, plug, and soil core were carefully dug out. The excess soil was cut away, smoothed, and leveled with the end of the cylinder. The hydraulic jack and special bracket were then employed in extracting the soil core (fig. 5). The core was forced out of the cylinder and carefully sliced off by 1-inch segments (fig. 6) and placed in a separate container for storage and analysis.

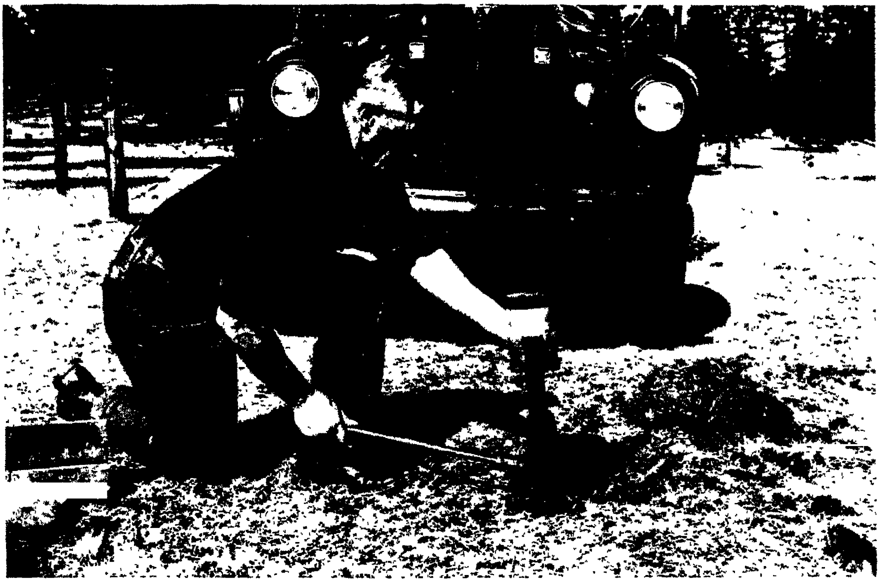

FIG. 5. SOIL CORE PARTLY EXTRACTED FROM SAMPLING CYLINDER THROUGH USE OF THE HYDRAULIC JACK, TUBE PLUG, AND SPECIAL BRACKET

INSTRUMENTAL ERROR AND SAMPLE VARIATION

It is almost impossible to design an experiment in which the variations attributed solely to the volume-weight sampler can be segregated. Each replicated sample will contain soil variation due to position, which usually exceeds that caused by the measuring instrument. Some figures, however, are presented which give a good indication of the reliability of this equipment.

Volume-weight figures obtained on one soil type in California and Texas are presented in table 2. These samples were obtained with the $3\frac{5}{8}$-inch diameter tube and varied from 4 to 6 inches in length. Three to four samples were taken at each indicated depth in one excavation in each type. The standard deviation is given for each average volume weight. These figures indicate that consistent results can

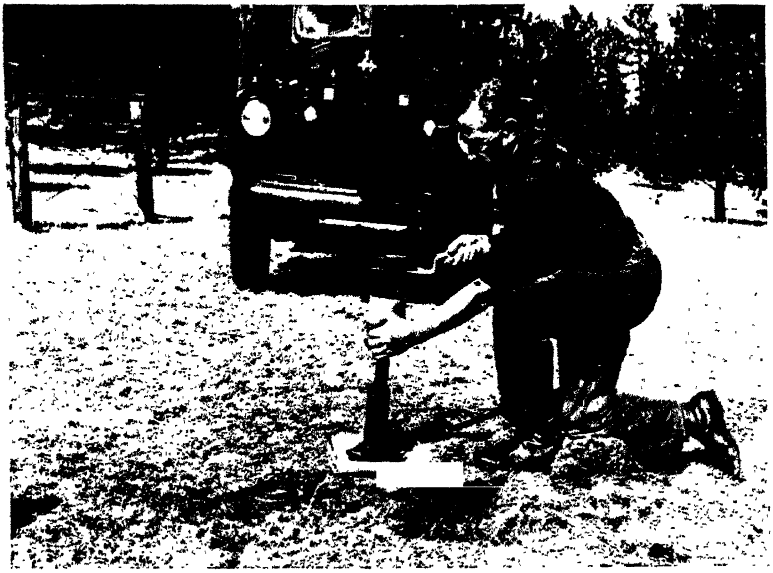

FIG. 6. SLICING OFF 1 INCH OF SOIL CORE AT A TIME

Soil is sandy loam alluvium derived from Pikes Peak granite with about 30 per cent gravel larger than 2 mm.

TABLE 2

Reliability of volume-weight samples taken in agricultural soils in California and Texas

HORIZON	SOIL DEPTH *inches*	TEXTURE	VOLUME WEIGHT	STANDARD DEVIATION ±
Moreno loam—San Jacinto Basin, Calif.				
A	4–8	Loam	1.40	0.009
	8–12	Loam	1.53	0.013
	12–22	Silt loam	1.23	0.010
C	22–32	Loam	1.31	0.008
	32–53	Fine sandy loam	1.37	0.013
	53–60	Fine sandy loam	1.38	0.004
	60–72	Fine sandy loam	1.41	0.013
	72–76	Loam	1.32	0.012
	76–80	Fine sandy loam	1.42	0.004
Lewisville silty clay—Seguin, Tex.				
A_1	0–8	Silty clay	0.95	0.020
A_2	8–24	Silty clay	1.24	0.004
B_1	24–36	Clay	1.31	0.006
B_2	36–60	Silty clay	1.48	0.008

be obtained on agricultural soils relatively free of gravel. Close agreement between replications was also obtained on agricultural sandy loam and loamy sand.

An indication of the instrumental error on coarse mountain range and timbered soils was obtained in the Rocky Mountains about 25 miles northwest of Colorado Springs. The sampled area included three of the 300- to 400-acre experimental pastures of the Rocky Mountain Forest and Range Experiment Station. The soil is alluvium derived almost entirely from Pikes Peak granite. The texture is a sandy loam with gravel larger than 2 mm. ranging from 3 to 60 per cent and averaging 27 per cent. Volume-weight samples were taken in 1946 in connection with an infiltration study employing a portable artificial rainmaker.

The experimental design included pastures of three grazing intensities: heavy, moderate, and light. Sampling was stratified in each pasture by three areas (upper, middle, and lower slope) and by three cover types (timber-litter, timber-grass, and grassland). Two volume-weight samples were obtained randomly at each infiltration plot, one in the upper half and one in the lower end of the $2\frac{1}{2}$-square-foot plots. Samples were taken by 1-inch increments to the 3-inch depth after soils had drained to the field capacity. Six soil samples at each of 54 infiltration plots sampled 27 conditions.

TABLE 3

Mean volume weights and deviations for upper and lower plot positions by cover type and depth

COVER TYPE	DEPTH					
	0–1 in.		1–2 in.		2–3 in.	
	Upper position	Lower position	Upper position	Lower position	Upper position	Lower position
	Volume weight					
Timber-litter	1.15	1.17	1.44	1.37	1.42	1.42
Timber-grassland	1.20	1.19	1.51	1.52	1.50	1.51
Grassland	1.21	1.28	1.49	1.44	1.50	1.46
	Standard deviation ±					
Timber-litter	0.13	0.12	0.14	0.14	0.10	0.15
Timber-grassland	0.12	0.17	0.10	0.13	0.10	0.11
Grassland	0.15	0.18	0.10	0.15	0.13	0.14

An analysis was made of the main factors influencing volume weight as well as their interaction one upon the other. The interrelation of the number of plots, the position of the samples within the plots, and the depth to which the samples were taken formed the basis for approximating the instrumental error. The standard deviation was ±0.093, giving a coefficient of variation of 6.7 per cent. This coefficient may appear fairly large because it includes variations due to soil differences between any two locations as well as instrumental error. In such a coarse-textured soil, large variations may be expected, particularly in 1-inch cores with soil volumes of only 250 cc. In addition, tree and herbaceous roots and animal burrows contributed to sampling error.

Some idea of variation between positions, cover types, and soil depths is given in table 3. Since volume weight varied only with cover type and depth, the standard deviations within these groupings eliminate their effect and approach the instrumental error. These deviations also include all variations between plot locations not attributed to cover type. In the grassland and timber-grassland types, sampling error averaged higher for the surface inch of soil than for deeper layers.

The consistency of results and the small instrumental error do not in themselves indicate entire freedom from bias. The latter can be determined only by a comparison of different methods. Comparisons were made between the tube and the clod-paraffin method, a modification of that described by Shaw (9). Large clods of soil of similar volume size to that obtained with the tube were used in the paraffin-immersion method. Soil samples were taken from adjacent positions at a single location in each type so as to minimize variations due to soils. These comparisons are presented in table 4 and show relatively close agreement between methods. The differences were within sampling variation, and no consistent bias was indicated.

TABLE 4

Comparison of paraffin-immersion and tube methods of determining volume weights

Placentia sandy loam—near Banning, Calif.

HORIZON	SOIL DEPTH	TEXTURE	WILTING POINT	VOLUME WEIGHT	
				Paraffin-immersion	3⅝-inch tube
	inches		*per cent*		
A	8–13	Sandy loam	4.0	1.67	1.63
B	13–24	Sandy clay loam (claypan)	6.2	2.03	1.96

Martinez clay—near Uvalde, Tex.

HORIZON	SOIL DEPTH	TEXTURE			FIELD CAPACITY	VOLUME WEIGHT	
		Sand	Silt	Clay		Paraffin-immersion	3⅝-inch tube
	inches	Per cent	Per cent	Per cent	*per cent*		
A	0–6	17	32	51	34.1	1.22	1.28
B_1	18–36	24	25	51	27.5	1.36	1.42
B_3	48–60	26	24	50	26.4	1.43	1.39

SUMMARY

A volume-weight sampler and procedure are described for determining porosity of soils. The instrument is simple and inexpensive and has been used successfully on both cultivated and mountain soils. The field procedure suggested for determining relative distribution of pore sizes is readily used in conjunction with artificial rainmaker and irrigation experiments. It can also be used after natural precipitation has saturated the soil horizon to be sampled. This field method is simple and rapid for surface soils, but more time-consuming for deeper soil horizons. The laboratory work involves merely weighing and oven-drying soil samples.

Some findings are given on expected variation between volume-weight measurements due largely to instrumental error. This error is small and indicates that consistent volume-weight measurements can be obtained with this instrument. The small error is due partly to the reduction of soil compression. Measurable compression of soil was eliminated by slowly forcing a tube 4.4 inches in diameter into the soil with a jack.

The reliability of this instrument for volume-weight measurements is indicated by the favorable comparison with values obtained by the paraffin-immersion method.

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EFFECTS OF FUMIGATION AND OTHER SOIL TREATMENTS IN THE GREENHOUSE ON THE FUNGUS POPULATION OF OF OLD CITRUS SOIL[1]

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Continuous cropping of the soil to the same plant often leads to a falling off in yields. In many instances this condition cannot be corrected by fertilization and is referred to as "soil sickness." Certain investigators are of the opinion that "soil sickness" is caused primarily by a build-up of detrimental organisms in the soil (1, 2, 3, 9, 10, 13, 17). In this connection many citrus growers of southern California have noted that trees of a second or third planting in old groves do not grow so well as those of the original planting or as plantings of similar trees on noncitrus soil. The condition is sometimes referred to as "slow decline of citrus," or as the effect of "citrus-sick soil."

In greenhouse experiments (21), sour and sweet orange seedlings made approximately 50 to 175 per cent more growth in soil from areas which had never been cropped to citrus than in old citrus soil from adjacent areas which had supported citrus trees 40 to 70 years. The seedlings growing in the old citrus soil did not respond to soil applications of phosphorus, potassium, magnesium, copper, zinc, boron, or manganese. The roots of the seedlings growing in the old citrus soil showed considerable decay, whereas those in noncitrus soil showed very little.

In a survey of the saprophytic fungus population of the soil, certain fungi were found to be more prevalent in old citrus soils than in adjacent noncitrus soils (20). One of these species, a strain of *Fusarium solani*, was repeatedly isolated from surface-sterilized feeder roots. This organism may be a secondary invader following primary infestation by the citrus root nematode, *Tylenchulus semipenetrans* Cobb, which has been found in considerable concentration in the feeder roots of citrus trees growing in old citrus soils (4, 7, 24); or following primary infection by the pathogenic fungus *Phytophthora*, which also has been found in old citrus soils (8, 16). Pure culture studies not yet published indicate, however, that *F. solani* is able to penetrate and decay the root tips of young, developing citrus seedlings. Furthermore, in greenhouse and sand-culture studies, cropping to citrus seedlings for 18 months had a pronouncedly depressing effect on a second planting of the same crop. A fungus population similar to that in citrus-sick soils developed in the sand, but no citrus root nematodes could be found. In addition to *F. solani*, several other species of *Fusarium*, a *Phytophthora* sp., *Thielaviopsis basicola*, and *Pyrenochaeta* sp. have been isolated from surface-sterilized roots.

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It is very probable that the saprophytic fungus population of the soil is for the most part either beneficial or harmless to plant growth. Under continuous cultivation of the same plant, however, it is possible for a microbial balance to become established which may be detrimental. Fungi and other microbes are found growing in close association with plant roots. Some produce antibiotic substances (27). If a type producing such a substance were to become established in close contact with the plant root, it is reasonable to hypothesize that root function might be impaired. Moreover, certain fungi, after continuous growth in the root vicinity, may become increasingly virulent, encroach more and more on the root hairs and outer root cells, and thus adversely affect the plant.

Recently, considerable attention has been given to biological control for combating undesirable organisms in the soil (5, 6, 9, 10, 15, 19, 28, 29, 30). Treating the soil with organic materials or otherwise favoring the growth of a different soil population may alter the detrimental balance or induce destruction of the harmful species by antagonistic forms. Partial soil sterilization may likewise improve plant growth, not only by destroying detrimental organisms but also by changing the microbial balance so that antagonistic forms can establish themselves.

Waksman and Starkey (25) reported that fungi are almost completely destroyed by volatile soil fumigants, but that they later re-establish themselves in larger numbers than before. These investigators noted that the types occurring after partial soil sterilization were limited to a few species. Katznelson and Richardson (14) found that certain *Penicillium* and *Plectonaemella* species increased in numbers in some partly sterilized soils. After treatment of soil with chloropicrin, Smith (22) observed that the fungus population which later developed consisted primarily of *Trichoderma* spp. Similarly, Ludwig and Henry (18) observed that platings of recontaminated steam-treated soil contained large numbers of *Trichoderma*. The presence of this fungus was thought to be an important factor in the reduced severity of attack of wheat seedlings by *Ophiobolus graminis*. On the other hand, after partial soil sterilization detrimental organisms may get started before antagonistic types and thus increase damage to plant roots (12).

Heavy fumigation has at times appreciably increased growth of young orange and lemon trees. In greenhouse tests (21) root rotting and the citrus root nematode were greatly reduced or were eliminated by soil fumigation. Growth was usually increased and occasionally more than doubled. Fumigation of old citrus soil did not return it to the status of a noncitrus soil, however. These results suggest that detrimental soil organisms are only partly responsible for reduced growth of citrus seedlings in old citrus soil, or that heavy soil fumigation does not kill all the harmful organisms, or, if it does, that conditions in the soil are favorable for re-establishment of the detrimental population.

It was thought important to determine whether the fungi of the soil were destroyed by the amounts of fumigants necessary to increase citrus growth in old citrus soils, and, if so, whether the same species or others would establish themselves after the fumigant had volatilized from the soil and after replanting to citrus or other crops. The effects of various other treatments on the fungus balance in the soil were also studied. These treatments included steam under pressure, Dithane (a fungicide), hexachlorocyclohexane (an insecticide), and leaching with distilled water, alcohol, 2 per cent sulfuric acid, 2 per cent potassium hydroxide, and with soluble salts. For comparison, some data on total numbers of bacteria in the soil are reported.

MATERIALS AND METHODS

For these experiments, old citrus soils were obtained from orchards which had supported citrus trees 40 to 70 years. Soils that had never been cropped to citrus (noncitrus) were obtained from adjacent areas. Each soil was screened, mixed, and fertilized before being placed in the experimental pots. Three-gallon pots were used, and all treatments were replicated.

Pots of soil were steam-treated at 15 pounds' pressure for 7 hours. Soils were fumigated by placing the proper fumigant in the pots near the bottom. This was done by forcing a small pipe into the soil by means of a center probe. The probe was then removed, and the fumigant was added by means of a pipette with a rubber bulb attached. The pipe was then removed, the hole covered, and 1 liter of distilled water applied to the surface to form a water seal. The pots were left exposed to the atmosphere without additional watering until planted to orange seedlings.

Dithane was added to the soil in solution. Hexachlorocyclohexane was mixed with the soil.

For the soil-leaching studies, pots of soil were leached with 6 gallons of 95 per cent alcohol per pot, or with distilled water for 6 weeks, with 2 per cent H_2SO_4 for 3 days, with 2 per cent KOH for 3 days, or with N NH_4Cl at pH 4.0 until the leachate was pH 4.0. After the soil had been leached with alcohol or distilled water, it was air-dried. The colloids of the remaining pots of leached soils were saturated with calcium by leaching with $CaCl_2$. The soils were then leached with distilled water at pH 7.0 to eliminate the chlorides.

When used, the amounts of the different materials added to the soil in the pots were as follows:

Material	*Amount per pot*
Carbon disulfide	12 ml.
Chloropicrin	4 ml.
Ethylene dibromide	2 ml.
Ethylene dichloride	20 ml.
D-D (dichloropropane and dichloropropylene mixture)	8 ml.
Dithane (disodium ethylene bisdithiocarbamate) 1–2,400 dilution	Soil saturation
Hexachlorocyclohexane	50 ppm. (active isomer)

After treatment, the soil was allowed to stand 1 month before either sour or sweet orange seedlings or tomatoes were planted. All plants were irrigated with distilled water.

Soils in the pots were sampled at intervals both before and after plants were growing in the pots. Each pot was sampled in two places with a sterile glass tube, to a depth of 1 to 4 inches. The first inch of soil was removed with a sterile spatula. At harvest times the soil samples were obtained by removing the roots from the soil and shaking off adhering soil into clean paper bags.

The numbers and types of saprophytic fungi in the soils were determined by the plate method, the advantages and disadvantages of which are well-known. Appropriate dilutions were made in sterile water blanks and plated in replicas of six, using Waksman's peptone dextrose agar (26) to which citrus-root extract had been added. The medium was adjusted to pH 4.0 with sterile H_2SO_4 just before the plates were poured. The plates were incubated at room temperature for 3 to 4 weeks. After 5 to 7 days, the colonies were counted and examined microscopically. Those which had not grown enough for identification were circled with a china-marking pencil and again examined after further incubation. Colonies which could not be identified on the plates were transferred to agar slants and plated on Czapek's, potato dextrose, and corn meal media. The various forms were identified, when possible, according to the classifications of Gilman (11) and of Thom and Raper (23).[3] Because of the extensive nature of the findings in this investigation, only part of them are presented in the tables.

RESULTS

Steam treatment of soil

The effects of the steam treatment on the approximate number and kind of fungi in an old citrus soil (Ramona clay loam) from the vicinity of Whittier, California, are reported in table 1. One month after treatment, part of the pots were planted to sour orange seedlings and part to tomatoes. Immediately after treatment no microbial colonies developed when soil from the center of the pots was streaked on agar plates. After 3 months and 9 months, during which the pots had been cropped, fungi were found to be present in the sterilized soil in numbers ranging from one to a hundred times that of the nontreated (control) soil. More than 20 species of fungi were identified in the control series, whereas only 1 to 5 species were found in the treated soils.

The kinds of fungi varied from one pot to another, even in a series of pots receiving identical treatment. In the tomato series, for example, after 3 months the population in one pot was almost entirely blue-green penicillia; in a second pot, *Fusarium oxysporum* and large numbers of *Mucor* spp. were present; in a third, the fungus population consisted largely of *Rhizopus nigricans*; and in still another, it consisted primarily of *Trichoderma lignorum*.

In the orange seedling series, after 3 months, the fungus population consisted of *R. nigricans*, blue-green penicillia, and *lignorum* in one pot, largely *Phoma* sp. in a second, and blue-green penicillia and *R. nigricans* in a third. After 9 months, the population in the first pot of soil had not changed, while in the other two only *T. lignorum* was found. With the exception of *Phoma* sp. all the fungi which became established after sterilization were found in the original soils.

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[3] Some of the forms were kindly examined by Ernst A. Bessey of Michigan State College, M. I. Timonin of the Canada Department of Agriculture, and E. A. Mason of the Imperial Mycological Institute, England.

Soil fumigation, fungicidal, and insecticidal treatments

The effects of several soil fumigants on numbers of bacteria and numbers and kinds of fungi in an old citrus soil before and after planting to sour orange seedlings are shown in table 2. After 2 weeks, no fungi were found in soil treated with D-D, as compared with more than 20 species in the untreated control soils, and 12, 8, and 6 species in soil treated with ethylene dibromide, carbon disulfide, and ethylene dichloride, respectively. The numbers of fungi in the treated soils increased, but after 8 months were still fewer than in the control soils. Even after bacterial numbers declined, the number of fungi remained relatively low. D-D was most effective in killing fungi and reducing the number of species in the soil. After 2 months the population in one pot consisted largely of *Penicillium* sp. 1, an unidentified species belonging to the Monverticillata group, while that in a

TABLE 1

Effect of steam under pressure on numbers and kinds of fungi in old citrus soil planted to tomatoes or sour orange seedlings 1 month after treatment*

FUNGUS	ORIGINAL SOIL	TOMATOES					CITRUS SEEDLINGS							
		Control soil	Treated soil				Control Soil		Treated soil					
		After 3 mos.	After 3 months				After 3 mos.	After 9 mos.	After 3 months			After 9 months		
		Pots 1 to 4	Pot 1	Pot 2	Pot 3	Pot 4	Pots 1 to 3	Pots 1 to 3	Pot 1	Pot 2	Pot 3	Pot 1	Pot 2	Pot 3
	Approximate number of fungi in thousands per gram of dry soil													
	62	45	335	54	288	790	85	61	53	250	265	82	186	174
	Approximate percentage concentration of fungi occurring on plates													
Fusarium oxysporum	2	10	0	11	0	0	15	16	0	0	0	0	0	0
F. solani	25	9	0	0	0	0	11	7	0	0	0	0	0	0
Mucor spp	3	<1	1	24	11	2	<1	2	0	0	0	0	0	0
Penicillia, blue-green	8	23	99	53	36	9	24	15	15	4	62	11	0	0
Phoma sp	0	0	0	0	0	0	0	0	0	92	0	0	0	0
Pyrenochaeta sp	21	3	0	0	0	0	5	6	0	0	0	0	0	0
Rhizopus nigricans	<1	7	0	8	53	1	3	1	70	4	26	61	0	0
Trichoderma lignorum	<1	<1	0	0	0	88	5	7	15	0	2	28	100	100
Fungus D1	6	2	0	0	0	0	4	5	0	0	0	0	0	0
Other species†	35	46	0	0	0	0	32	41	0	0	10	0	0	0
	Total number of identified species													
	25	23	2	5	3	4	21	23	3	3	5	3	1	1

* Ramona clay loam from depths of 3 to 24 inches.

† Including unidentified fungus colonies.

second pot was largely *Aspergillus sydowi*; after 4 and 8 months, both pots contained both species. After the other fumigation treatments, although there were differences between pots of the different treatments and of the same treatment, the main fungus species consisted of various combinations of *A. sydowi*, *A. versicolor*, *F. oxysporum*, *Penicillium nigricans*, blue-green penicillia, and *Penicillium* sp. 1. *Trichoderma lignorum* did not become established as it did in the steam-sterilized soil (table 1). With the exception of *Penicillium* sp. 1, all the fungi were found in the original soil. The total numbers of species in the fumigated soils increased with time, but even after 8 months there were fewer species in these soils than in the untreated soil.

TABLE 2

Effect of soil fumigants on numbers of bacteria and numbers and kinds of fungi in old citrus soil before and after planting to sour orange seedlings*

FUNGUS	ORIGINAL SOIL	UNTREATED CONTROL		D-D				ETHYLENE DIBROMIDE			CARBON DISULFIDE				ETHYLENE DICHLORIDE		
		Intervals after soil treatment															
		2 wk.	8 mo.	2 wk.	2 mo.† A	2 mo.† B	8 mo.	2 wk.	2 mo.	8 mo.	2 wk.	2 mo.† A	2 mo.† B	8 mo.	2 wk.	2 mo.	8 mo.
	Approximate number of bacteria in millions per gram of dry soil																
	12	11	8	20	27	40	8	49	25	6	39	50	42	13	35	25	8
	Approximate number of fungi in thousands per gram of dry soil																
	72	81	38	0	34	35	18	19	22	24	7	18	17	20	34	14	20
	Approximate percentage concentration of fungi occurring on plates																
Aspergillus sydowi	<1	1	5	0	0	84	13	4	3	3	3	0	0	13	0	2	3
A. versicolor	3	10	9	0	8	0	2	14	22	16	3	12	11	19	6	9	30
Fusarium solani	10	8	15	0	1	0	0	1	8	9	<1	5	0	11	0	8	6
Penicillia, blue-green	4	21	16	0	0	0	0	33	11	18	48	10	34	20	10	36	19
Penicillium nigricans	8	4	5	0	0	0	0	0	0	0	36	10	20	4	77	8	3
Penicillium sp. 1	0	0	0	0	71	12	75	0	0	0	6	42	0	0	0	0	0
Pyrenochaeta sp.	12	8	6	0	0	0	0	11	13	1	0	0	0	0	0	0	0
Trichoderma lignorum	<1	2	2	0	2	0	0	0	6	<1	0	6	0	1	0	1	0
Fundus D1	41	23	6	0	0	0	0	0	1	4	0	0	0	1	0	3	<1
Other species‡	22	23	36	0	18	4	10	37	34	48	10	15	35	30	7	33	39
	Total number of identified species of fungi																
	31	26	22	0	7	2	6	12	13	19	8	11	7	15	6	13	15

* Hanford sandy loam from depths of 3 to 24 inches. Citrus seedlings planted 1 month after soil was fumigated.

† Duplicate pots recorded separately.

‡ Including unidentified fungus colonies.

Similar results for a noncitrus soil also showed the D-D was more effective in reducing the numbers and kinds of fungi than was ethylene dibromide, ethylene dichloride, or carbon disulfide. In only one pot of soil, previously fumigated with carbon disulfide, did the total numbers of fungi surpass those in the control soil. The fungus populations which became established also differed between treatments and between individual pots receiving the same treatment. Even after 8 months the fungus population in some pots was different from that

TABLE 3

Effect of several soil fumigants and of the fungicide Dithane and the insecticide hexachlorocyclohexane on numbers of bacteria and numbers and kinds of fungi in old citrus soil before and after planting to sour orange seedlings*

FUNGUS	UNTREATED CONTROL		CARBON DISULFIDE		D-D				ETHYLENE DIBROMIDE		CHLOROPICRIN			DITHANE		HEXACHLOROCYCLOHEXANE	
	Intervals after soil treatment																
	5 days	6 mo.	5 days	6 mo.	5 days	1 mo.	3 mo.	6 mo.	5 days	6 mo.	5 days	3 mo.	6 mo.	5 days	6 mo.	5 days	6 mo.
	Approximate number of bacteria in millions per gram of dry soil																
	10	9	27	9	3	44	71	54	19	9	4	18	17	4	36	11	8
	Approximate number of fungi in thousands per gram of dry soil																
	63	50	1	12	0	18	920	165	20	16	0	0	1	0	24†	6	33
	Approximate percentage concentration of fungi occurring on plates																
Aspergillus sydowi	3	2	30	0	0	0	0	0	5	3	0	0	0	0	4	0	8
A. versicolor	7	14	40	3	0	0	0	0	14	20	0	0	0	0	23	12	14
Fusarium solani	13	24	0	6	0	0	0	3	11	24	0	0	0	0	17	18	15
Fusarium sp. 3	0	0	0	0	0	0	0	0	0	<1	0	0	0	0	2	40	0
Monotospora brevis	0	2	0	0	0	0	0	0	0	3	0	0	25	0	0	0	2
Oospora variabilis	3	3	0	0	0	0	0	0	6	1	0	0	0	0	15	0	7
Penicillia, blue-green	12	11	20	3	0	0	0	0	14	7	0	0	0	0	10	0	7
Penicillium sp. 1	0	0	0	0	0	0	0	0	0	0	0	0	75	0	0	0	0
Phoma sp.	0	0	0	88	0	0	0	0	0	0	0	0	0	0	0	0	0
Trichoderma lignorum	1	<1	0	0	0	82	96	82	1	8	0	0	0	0	0	0	1
Fungus D1	27	11	0	0	0	0	0	0	2	0	0	0	0	0	7	0	4
Other species‡	34	33	10	0	0	18	4	15	47	34	0	0	0	0	22	30	42
	Total number of identified species of fungi																
	23	25	4	5	0	2	2	4	20	21	0	0	2	0	13	5	19

* Hanford sandy loam from depths of 3 to 24 inches. Citrus seedlings planted 1 month after soil was treated.

† 450,000 yeasts per gram of dry soil.

‡ Including unidentified fungus colonies.

in the checks; in other pots it was almost the same as in the original soil. Several *Penicillium* sp., *Torula* sp. 1, *Mucor* spp., *F. solani*, and *Aspergillus niger* were the principal kinds established after fumigation. With the exception of *Penicillium* spp. 1 and 2, all were present in the original soil.

TABLE 4

*Effect of carbon disulfide on numbers of bacteria and numbers and kinds of fungi in old citrus soil and noncitrus (garden) soil planted to sour orange seedlings 1 month after treatment**

FUNGUS	OLD CITRUS SOIL						NONCITRUS SOIL						
	Untreated control		Carbon disulfide				Untreated control		Carbon disulfide				
	Intervals after soil treatment												
	1 mo.	9 mo.	1 mo.	3 mo.†		9 mo.	1 mo.	9 mo.	1 mo.†		3 mo.	6 mo.	9 mo.
				A	B				A	B			
	Approximate number of bacteria in millions per gram of dry soil												
	12	16	58	91	50	27	23	18	42	83	65	48	26
	Approximate number of fungi in thousands per gram of dry soil												
	15	34	6	41	6	14	15	19	7	270	16	16	13
	Approximate percentage concentration of fungi occurring on plates												
Aspergillus niger	1	9	0	0	0	9	3	13	0	<1	<1	0	2
A. versicolor	0	6	0	0	16	<1	5	2	12	0	8	4	12
Chaetomella sp	0	0	0	0	0	0	0	0	0	87	24	<1	0
Fusarium solani	38	21	98	12	84	58	10	23	13	<1	12	28	48
Penicillia, blue-green	0	8	0	0	0	8	14	4	22	<1	15	5	2
Phoma sp	0	0	0	79	0	0	0	0	0	0	0	0	0
Sclerotium sp	0	<1	0	0	0	0	15	2	8	2	13	36	7
Trichoderma lignorum	0	2	0	0	0	0	13	9	13	<1	2	16	1
Fundus D1	43	14	2	0	0	10	0	0	0	0	0	0	0
Other species‡	18	41	0	9	0	15	40	47	32	9	26	10	28
	Total number of identified species of fungi												
	10	14	2	3	2	7	15	16	9	9	14	13	13

* Yolo sandy loam from depths of 6 to 48 inches.

† Duplicate pots recorded separately.

‡ Includes unidentified fungus colonies.

Table 3 shows the effects of several fumigants and of the fungicide Dithane and the insecticide hexachlorocyclohexane on the fungus population of an old citrus soil.

Of the fumigants, chloropicrin and D-D were most effective in killing the soil fungi. In the D-D treated soil, *Trichoderma* spp. soon became established, and at 1, 3, and 6 months they were virtually the only fungi occurring on the plates from this soil. At 3 months, the fungi numbered more than 900,000 per gram of dry soil. In a previous experiment (table 2), *Trichoderma* spp. did not become established in the soil after D-D treatment except in very small numbers in one pot. Chloropicrin apparently eliminated the fungus population for more than 3

TABLE 5

*Effect of various leaching agents on numbers and kinds of fungi in old citrus soil and in noncitrus (garden) soil after planting to tomatoes**

FUNGUS	ORIGINAL SOIL	OLD CITRUS SOIL							NONCITRUS SOIL							
		Control	H_2O	Alcohol		H_2SO_4†	KOH†	NH_4Cl†	Control	H_2O	Alcohol	H_2SO_4†		KOH†		NH_4Cl†
				A	B							A	B	A	B	
	Approximate number of fungi in thousands per gram of dry soil at harvest															
	42	78	98	22	15	80	73	22	75	90	6	23	5	50	56	60
	Approximate percentage concentration of fungi occurring on plates at harvest															
Aspergillus candidus	0	1	0	0	0	0	0	0	0	0	0	0	40	0	0	0
A. sydowi	<1	0	<1	0	0	0	1	0	0	0	0	0	18	0	0	0
Cylindrocarpon radicicola	0	0	0	0	0	0	0	0	2	19	0	93	0	0	0	4
Fusarium solani	11	6	4	28	10	0	2	5	1	6	17	0	0	0	0	3
Fusarium sp. 3	2	3	0	0	0	0	3	3	1	2	47	0	0	3	0	2
Gliocladium penicilloides	0	0	0	48	0	1	44	2	0	2	3	0	0	45	0	0
Nematagonium sp.	0	0	0	5	0	0	12	0	0	0	0	0	0	0	0	0
Penicillia, blue-green	3	16	13	0	0	0	0	1	18	15	3	0	0	16	6	1
Penicillium nigricans	24	19	17	12	0	93	19	55	4	0	0	0	0	13	0	1
P. restrictum	2	0	0	0	0	0	0	0	26	8	3	0	0	0	0	0
Pyrenocheta sp.	12	12	38	0	0	0	0	0	0	0	0	0	0	0	0	0
Torula sp. 1	0	0	0	0	0	0	0	0	2	<1	0	0	0	0	79	39
Trichoderma lignorum	<1	8	6	0	90	3	2	4	5	0	12	0	12	7	15	0
Fungus D1	28	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0
Other species‡	18	28	19	7	0	3	17	30	37	48	15	7	30	15	0	50
	Total number of identified species															
	18	16	13	4	2	4	9	11	21	16	8	3	6	7	3	13

* Hanford sandy loam from depths of 6 to 48 inches. Tomatoes were grown approximately 4 months.

† After initial treatment, soil colloids were saturated with calcium.

‡ Including unidentified fungus colonies.

months, although orange seedlings were growing vigorously in the soil for 2 of the months. At 6 months, a count of only 1,000 fungi per gram of dry soil was obtained. The predominant species in the carbon-disulfide-treated soil were *A. versicolor*, blue-green penicillia, and *Phoma* sp.

Dithane initially reduced the mold count to nought, but at 3 and 6 months fungi were again present in approximately half the numbers found in the control soils. The kinds which became established were approximately the same as in the original soil, with the exception of Fungus D1 (20), which was present in smaller numbers, and of *Oospora variabilis*, which was present in larger numbers. Ethylene dibromide and hexachlorocyclohexane, in the amounts used, reduced the numbers of fungi by two thirds or more but had little effect on kinds.

TABLE 6

*Effect of various leaching agents on numbers and kinds of soil fungi in old citrus soil and noncitrus (garden) soil after planting to sour orange seedlings**

FUNGUS	ORIGINAL SOIL	OLD CITRUS SOIL						NONCITRUS SOIL					
		Control	H_2O	Alcohol	H_2SO_4†	KOH†	NH_4Cl†	Control	H_2O	Alcohol	H_2SO_4†	KOH†	NH_4Cl†
	Approximate number of fungi in thousands per gram of dry soil at harvest												
	42	86	95	235	255	135	115	86	80	21	80	115	65
	Approximate percentage concentration of fungi occurring on plates at harvest												
Aspergillus ochraceus	<1	0	0	0	0	0	0	4	0	18	0	0	0
A. versicolor	3	0	2	48	0	0	0	6	16	2	0	0	0
Fusarium solani	11	8	21	21	1	2	9	4	18	40	6	4	36
Fusarium, sp. 3	2	4	0	2	1	13	0	0	2	0	0	1	0
Penicillia, blue-green	3	4	6	0	0	0	0	22	11	20	0	0	4
Penicillium nigricans	24	30	31	0	98	85	84	0	15	10	40	86	30
P. restrictum	2	0	0	0	0	0	0	36	2	0	0	0	4
Pyrenocheta sp.	12	10	8	0	0	0	2	0	0	0	0	0	0
Spicaria sp.	0	0	0	0	0	0	0	0	0	0	40	0	0
Trichoderma ligornum	<1	2	2	3	0	0	0	2	4	0	12	8	0
Fungus D1	28	14	14	15	0	0	0	0	0	0	0	0	0
Other species‡	16	28	17	11	0	0	5	26	32	10	2	1	24
	Total number of identified species												
	18	13	12	6	3	3	6	14	14	8	4	5	9

* Hanford sandy loam from depths of 6 to 48 inches. Citrus seedlings were grown approximately 9 months before being harvested.

† After initial treatment, soil colloids were saturated with calcium.

‡ Including unidentified fungus colonies.

The effects of carbon disulfide on the number of bacteria and on the numbers and kinds of fungi in an old citrus soil and in a garden soil from the vicinity of Santa Paula, California, are presented in table 4. As in the previous experiments, numbers and kinds of fungi were initially reduced. With two exceptions, the numbers remained below those in the control. The main species to become established after fumigation were *Phoma* sp., *Chaetomella* sp., *Fl solani*, *Sclerotium* sp., and blue-green penicillia. *Phoma* sp. and *Chaetomella* sp. were not found in the original soil.

Soil leaching

The effects of leaching on the fungus population in old citrus and noncitrus soils from Fullerton, California, are shown in tables 5 and 6. Only figures for the harvest date are given. Leaching with distilled water for 6 weeks had little effect. All the other treatments produced an effect similar to that of carbon disulfide or D-D. Initially, the fungi were reduced in numbers and kinds. After 4 months in the tomato series and 9 months in the orange seedling series, the population was still very different from that of the controls. The nature of the fungus population varied between pots of identical treatment and of different treatments. In some pots total numbers of fungi were much higher than in the controls; in others they were lower. The fungus most commonly established was *P. nigricans*, which was present in relatively high concentration in the check soils. *Pyrenochaeta* sp. and Fungus D1, which were common in the original old citrus soil, were eliminated and did not re-establish themselves in the leached soils. *Fusarium solani* returned to some of the soils but not to others. *Aspergillus candidus*, *A. sydowi*, *A. versicolor*, *Fusarium* sp. 3, *Penicillium restrictum*, *T. lignorum*, *Torula* sp. 1 and *Nematagonium* sp. became established in relatively high concentration in one or more treated pots.

In additional tests, not represented in the tables, similar results were obtained. In one soil a *Phytophthora* sp. and *T. basicola* became established after fumigation. In this same soil, the addition of alfalfa meal caused death of all the seedlings during the early stages of decomposition of the alfalfa. *Phytophthora* sp. was isolated from root and stem lesions. During the later stages of decomposition of the alfalfa, *Phytophthora* sp. could not be found.

In all the tests, when *F. solani* or *F. oxysporum* became re-established as the predominant species, the total numbers were relatively low.

DISCUSSION

Treatment with various soil fumigants, with Dithane, hexachlorocyclohexane, steam, and by leaching with alcohol, 2 per cent H_2SO_4, 2 per cent KOH, or with soluble salts, markedly affected the fungus population of the soil. As reported by others for similar treatments (25), the fungi were initially destroyed or reduced to very low numbers. Later they re-established themselves. Usually, the fungi which became established after treatment in any one soil represented comparatively few species. Even though plants were growing vigorously in the soil, the fungus population 9 months after treatment generally differed from that of untreated soil. The numbers and kinds of fungi differed greatly in pots of the different treatments and in replicate pots of the same treatment. In some pots one, two, or three species constituted the whole mold population; in others ten or more species became established. In some pots the fungi were the same types found in abundance in the original soil, in other pots fungus types found in relatively small numbers in the original soil became abundant, and in still other pots species not found in the original soil became the dominant species. It appears probable that in some pots the initial treatment failed to kill all the fungi, and these fungi later developed in relative abundance, whereas in other pots all the fungi were killed and introduced fungus types became established as dominant species. Laboratory studies using sterile techniques support these views.

The following fungi established themselves as dominant species in one or more soils after partial soil sterilization:

Occasionally

*Aspergillus candidus**
A. niger‡
A. ochraceus‡
A. sydowi†
Chaetomella sp.*
Cyclindrocarpon radicicola‡
Fusarium sp. 3‡
Fusarium sp. 5*
*Gliocladium penicilloides**
Monotospora brevis‡
Nematagonium sp. *
Oospora variabilis‡
Penicillium humicola‡
Penicillium sp. 2*
Phoma sp.*
Phytophthora sp.*
Rhizopus nigricans‡
Sclerotium sp.‡
Spicaria sp.*
*Thieleviopsis basicola**
Torula sp. 1†
Torula species*
*Tricotheceum roseum**
Fungus D1†

Commonly

Aspergillus versicolor†
Fusarium oxysporum†
F. solani†
Mucor spp.‡
Penicillia, blue-green†
Penicillium nigricans†
P. restrictum†
Penicillium sp. 1*
Pyrenochaeta sp.†
Trichoderma lignorum‡

* Found only rarely or not at all in original soil.
† Found in relatively large concentration in original soil.
‡ Found in relatively small concentration in original soil.

Obviously, one cannot predict what the fungus population of a soil will be after treatment with a material that initially kills all or most of the soil fungi.

The greater number of species which most commonly developed after a partial soil-sterilization treatment were forms that had constituted a major portion of the population of the original soil. This would indicate either that some of the spores or mycelia of these forms survived the soil treatment and were able to develop again before other competing species could become established, or that conditions within the treated soil were favorable for their re-establishment and development. *Fusarium solani*, *F. oxysporum*, and *Pyrenochaeta* sp. were dominant in the original old citrus soils. The growth of citrus in the soil favors the development of these forms (20). When they became the most common types after partial sterilization, the total numbers of fungi remained relatively low. Fungus D1 (20), another fungus commonly found in old citrus soils, was in most tests largely eliminated for the duration of the experiments by the various treatments.

In studies not reported in this paper, incoulation of noncitrus soil with the dominant fungus species of old citrus soil did not result in the establishment of the introduced species in the soil. After citrus was grown in the noncitrus soil for a year or more, however, these forms established themselves without artificial inoculation.

Thus, in the experiments reported, two factors influenced the type of fungus population in the soil, namely, (*a*) the partial soil-sterilization treatment and (*b*) the growth of the plants in the soil. In most pots the former exerted the greater influence in the course of the experiments.

The fact that so many different fungus populations may become established after partial soil sterilization may explain why inconsistent results are sometimes obtained when soil is treated for a certain pathogenic fungus. In one soil a population antagonistic to the pathogen may develop, whereas in another soil a population favorable to the growth of the same pathogen may become established.

There was little correlation between total numbers of bacteria and fungi in the treated soils. The numbers of bacteria rapidly reached a maximum, then leveled off and decreased. In some pots the maximum numbers of fungi corresponded with the maximum number of bacteria; in others, the maximum numbers of fungi developed after the bacterial numbers began to decline. In replicate pots of the same treatment, the bacterial numbers were usually similar. This was not the case with the fungi: in one pot the number of fungi might remain less than in the control, whereas in a duplicate pot the number might be five to ten times that of the control.

In some of the treated pots of soil, the fungus species which first became the dominant types remained dominant for the rest of the experiment. In other treated pots, a succession of forms occurred. In one pot of soil in the steam-treated series, for example, after 3 months, *R. nigricans*, blue-green penicillia, and *T. lignorum* were found. After 9 months, these three species were still the only fungi found in this pot of soil, and the relative concentration of each species was almost identical with that at 3 months. In another pot *Phoma* sp., and in a third pot blue-green penicillia and *R. nigricans*, were the primary forms at 3 months; at 9 months only *T. lignorum* was found in both pots. This latter succession of forms is similar to that observed by Ludwig and Henry (18). In various fumigated soils, the following succession of species occurred: *A. sydowi* and *A. versicolor*, followed by *Phoma* sp.; *Phoma* sp. followed by *F. solani* or *T. lignorum*; *Chaetomella* sp. followed by *A. sydowi*, *A. versicolor*, and *F. solani; R. nigricans* and *Penicillium* spp. followed by *T. lignorum*; and *Penicillium* sp. 1 followed by other *Penicillium* spp., *Aspergillus* spp., and *Fusarium* spp.

Of the various soil treatments, steam under pressure, fumigation with chloropicrin and D-D, and leaching with 2 per cent H_2SO_4 and with 2 per cent KOH were most effective in destroying the fungi and in altering the nature of the subsequent fungus population of the soil.

In view of the fact that the environmental conditions of the soil were greatly altered by removing the soil from the field, from various depths, and placing it in pots in the greenhouse, the nature of the fungus population in the control soils changed surprisingly little. The predominant species remained the same in most pots. In some pots, however, there was a tendency for *Pyrenochaeta* sp. and fungus D1 to decrease in relative concentration while some of the penicillia increased. This may be explained by the fact that the two first-named species are found in relatively greater concentration in the subsoil than in the surface soil. In the noncitrus soils cropped to orange seedlings, *Fusarium* spp. increased in relative concentration probably as a result of the growth of citrus seedlings in the soil.

All treatments except those with Dithane, hexachlorocyclohexane, and steam appreciably increased growth of orange seedlings in old citrus soils and had relatively little effect on growth in most noncitrus soils. Dithane, hexachlorocyclohexane, and steam decreased growth in noncitrus soils. In general, there was no definite correlation between the fungus population of the soil in the treated pots and plant growth. In those series in which the *Fusarium* spp. became the primary forms after treatment, however, plant growth was usually less than in those series in which other fungi constituted the major part of the population. Root decay was usually decreased by the partial sterilization treatments.

These observations and the fact that the fungus population in all the treated soils was temporarily, or for the length of the experiment, greatly altered, suggest that a detrimental soil population is partly responsible for poor growth of citrus seedlings in old citrus soils, and that the change in microbial balance resulting from partial soil sterilization may be one factor involved in the improvement in plant growth. On the other hand, the fact that the fungus population was completely changed in many treated soils and the growth of orange seedlings still was not so good as in the noncitrus soils, although better than in the controls, suggests that factors other than the soil fungi also are partly responsible for reduced growth in old citrus soils. It should also be noted that a great difference in the qualitative and quantitative nature of the fungus population of a particular soil cropped to a single plant may exist without altering the growth of the plant.

SUMMARY

Treatment of old citrus and noncitrus soils by steam under pressure or by leaching, or with various fumigants, fungicides, or insecticides, followed by cropping with sour or sweet orange seedlings or with tomatoes, markedly affected the nature of the fungus population of the soil.

After initial destruction or near destruction of the fungus populations of these soils, fungi again established themselves, although the kinds and numbers established varied greatly between treatments and between replicate pots of the same treatment, and represented few species in comparison with the wide variety originally present. One or several of 10 fungus species commonly became dominant and one or more of 24 species occasionally became dominant. Some of the species were present in relatively large concentration in the orignal soil, some in relatively small concentration, and others were found only rarely or not at all in the original soil. In some pots, species which first became established after chemical treatment remained the dominant types for the duration of the cropping experiment (9 months), while in other pots a succession of forms occurred. Although some fungus species became established more frequently than others, it would be difficult to predict the effect of various partial soil sterilization substances on the exact nature of the fungus population of the soil.

For destroying soil fungi and altering the nature of the subsequent fungus population, steam under pressure, fumigation with chloropicrin or D-D, or leaching with 2 per cent H_2SO_4 or with 2 per cent KOH was more effective than fumigation with carbon disulfide, ethylene dichloride, or ethylene dibromide, than treatment with Dithane or hexachlorocyclohexane, or than leaching with ammonium chloride at pH 4.0.

The possible significance of the effect of altering the microbial equilibrium of the soil by partial soil sterilization on the growth of citrus in old citrus soils is discussed.

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SIGNIFICANCE OF CARBONATES IN IRRIGATION WATERS

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In terms of the difficulty and cost of reclamation and the severity of its effects, black alkali continues to occupy a prominent position among the unfavorable consequences of irrigation. Black-alkali soils are notably low in organic matter and characteristically poor in permeability to water; often there is an accumulation of salt, and surviving plants are likely to be chlorotic. It is now well known that for each of the foregoing characteristics there are responsible antecedent properties: the pH of black-alkali soil is in excess of 8.3 or 8.4, sodium is the predominant exchangeable base, the nutrients iron and phosphorus have low solubility, and further, a condition which provides for the term "black-alkali," organic matter tends to dissolve in alkaline solutions. The extent of the last effect is influenced in some measure by the kind of anions in the soil solution.

The association of black-alkali formation with sodium carbonate and bicarbonate of irrigation waters, as originally pointed to by E. W. Hilgard and R. H. Loughridge, was utilized by Stabler (10) as early as 1911 in his rating formulas for irrigation waters, and then, for reasons that are not obvious, the relation was largely neglected. In 1941 a number of opinions in this field were advanced in a set of discussions of a paper by Hill (6) in which, for the purpose of a geochemical chart, sulfates were grouped with carbonates. Stabler recalled (10) that in accord with Hilgard he had rated Na_2CO_3 as being twice as undesirable as NaCl and ten times as undesirable as Na_2SO_4. M. R. Lewis in a consideration of reclamation, agricultural production, and pH values of soils of the Pacific Northwest expressed the view that the carbonates and bicarbonates were too important to be grouped with sulfates. Lewis J. Alexander, whose interests were in waters of the Los Angeles Coastal Plain, proposed a water classification in which one type would be those waters whose CO_3 plus HCO_3 exceeded both Na plus K and Cl plus SO_4. C. S. Scofield asserted that the harmfulness of carbonate and bicarbonate had been overrated and that sodium was no less harmful when it occurred with sulfate, chloride, and nitrate than with carbonate.

Carbonates and bicarbonates of irrigation waters are discussed in this paper from two viewpoints: first, the relation of these ions to black-alkali formation, to which reference has been made; second, and of perhaps more widespread and greater day-to-day significance, the relation of the quantity of these ions in a water to the magnitude of the changes in the percentage sodium which can take place as the irrigation water becomes the soil solution and undergoes concentration by evaporation and by uptake of water by the plant.

RELATION OF CO_3^{--} AND HCO_3^- TO BLACK-ALKALI FORMATION

If a water supply contains more carbonate and bicarbonate than calcium and magnesium then, after evaporation and plant uptake have resulted in precipitation of the calcium and magnesium as carbonate salts, the residue of carbonate is paired with sodium. This sodium carbonate is Palmer's (9) primary alkalinity. For descriptiveness it will be referred to in this paper as "residual sodium carbonate." As the concentration of sodium carbonate increases, so also does the pH of the soil and the intensity of the plant and soil symptoms which are characteristic of black alkali. The replacement by sodium of the exchange calcium and magnesium of the soil brings about progressive destruction of particle aggregates and, with particle dispersion, impermeability, provided the soil solution is not very saline. A sodium soil may be permeable to saline water and yet be extremely impermeable to rain.

So far as is known, the anions are without influence on the base equilibrium between solution and clay. In other words, leaching or treating a soil with a sodium chloride or sodium sulfate water will have the same effect on exchange as sodium carbonate if the percentage of sodium in each is equal and is sufficiently in excess of calcium and magnesium.

CHANGES IN PERCENTAGE SODIUM IN WATER

But to come to the second point which is to be discussed in this paper, the absorbed calcium and magnesium of the soil may also be replaced by sodium when the irrigation water contains more calcium and magnesium than sodium. For this to take place, it is only necessary that the water contain sufficient $CO_3 + HCO_3$ to precipitate enough calcium to raise the sodium percentage to a point where exchange can progress. For this to occur, the water has to be used sparingly enough that during passage through the soil its volume is reduced to the point that much of the calcium and magnesium are precipitated as carbonate salts. The difference between this latter type of water, which would not give carbonate alkalinity, and the black-alkali type thus rests on whether the HCO_3 plus CO_3 is less or greater than Ca plus Mg.

It should be evident from the foregoing that a low percentage sodium value for an irrigation water does not necessarily provide assurance against calcium displacement and against soil dispersion and impermeability. Such being the case, there is an obvious need of a means for extending and safeguarding the usefulness of percentage sodium as an index of the effect waters may have on soil permeability. Later in this paper a means for this is suggested and applied to a number of irrigation waters. Had the writer appreciated the fairly obvious dependence of a given sodium percentage on the concentration of bicarbonate at the time of his early paper (2) on the irrigation waters of the San Joaquin Valley of California, he would have understood better some of the conditions he saw there. The custom of calculating the percentage sodium for each water analysis was introduced in that paper.

Without an adequate appreciation of the importance of the anions in shaping changes in the composition of waters as they become the soil solution and affect soil permeability, about all the writer could conclude as a consequence of his efforts to associate water chemistry with crop and land conditions was that the hazards of using a water increased rapidly as the sodium percentage increased above 60 and decreased as the percentage fell below that level. Recently the relationship has been enlarged (11) with the suggestion that soils "which naturally have good structure and permeability may not give trouble even if the sodium percentage is as high as 75 in the irrigation water, providing the total salt content is low." But here again the writers were confronted with uncertainties and phrased their statement with care.

Although Kelley (8), in dealing in 1940 with various features of water quality, did not carry his discussion to the point of analyzing the bearing of the concentrations of the several anions of water on the effects of varying proportions of sodium, he did point out that

> . . . the ratio of sodium to calcium in the actual soil solution may become substantially greater than it is in the water applied. This is due to the fact that calcium is absorbed by crops, and is therefore removed from the soil to a much greater extent than sodium; or it is precipitated as insoluble carbonate, which produces the same type of effect on this ratio.

Kelley reported that little sodium will be absorbed by the soil unless the ratio of sodium to calcium in the soil solution is greater than 2:1. A great preponderance of irrigation waters annually add so much more calcium to the land than the plants accumulate and so much of this is returned in the plant to the land that this factor can usually be neglected, but sight should not be lost of Kelley's second point.

To follow the discussion of waters in terms of their effects, there appear to be three types that are of special significance in the present connection. These three types can give rise, in time and absence of good drainage or when used too sparingly, to three corresponding types of soil, each of which is undesirable:

1. *Calcium saline soils.* These are produced by waters that are much higher in Ca + Mg than in $HCO_3 + CO_3$ and which have relatively low percentage sodium values ($Ca + Mg > HCO_3 + CO_3$ and $Ca + Mg > Na$). Such waters are without ill effects on soil structure. If salt accumulates, because of insufficient leaching of the root zone, the land can be readily reclaimed by draining and leaching.
2. *Sodium saline soils.* These are produced by waters that initially, or after partial evaporation and the precipitation of $CaCO_3$, have high percentage sodium values but which contain no residual sodium carbonate ($Ca + Mg =$ or $> HCO_3 + CO_3$ and $Ca + Mg < Na$). When these waters are used, the absorbed Ca and Mg of the soil is replaced progressively by Na as the percentage of sodium in the soil solution rises sufficiently high. Unless the water supply, or the soil solution, remains fairly saline, soil permeability will deteriorate. Although it might be properly argued that alkali conditions can result from the hydrolysis of sodium clay developed by the action of neutral sodium salts, Kelley and Brown (7) have pointed out that sodium soils are almost impermeable to any water sufficiently low in salt to cause hydrolysis of the sodium clay. Even though such hydrolysis is possible in the laboratory it seems probable that without the action of water containing residual sodium carbonate, black-alkali formation is extremely rare under field conditions.
3. *Alkali soils, saline or nonsaline.* Development of strong alkalinity may be expected when irrigation waters containing more $HCO_3 + CO_3$ than Ca + Mg ($Ca + Mg < HCO_3 + CO_3$) are used so sparingly that little leaching occurs. On the other hand, if sodium is not too greatly in excess of calcium and magnesium and enough of such water is used that the drainage continues to contain a substantial proportion of Ca and Mg there may be no ill effects.

It is only an occasional water supply that contains sufficiently high concentrations of salts to be directly harmful to plants. Also the waters which in their initial state have sodium percentages high enough to displace much calcium are in the minority. For these reasons, the interpretive value of water analyses becomes dependent not alone, or perhaps not so much, on the concentrations and proportions of ions found in the initial water as on what these concentrations and proportions will be at successive stages of volume reduction. As the irrigation water becomes the soil solution and progressively loses volume during its passage through the root zone, many changes will occur. If there is some movement through the root zone, the water may emerge with a half, a tenth, a hundredth, or less of its initial volume. This residual volume may contain nearly all of the initial chloride but there may be large increases or decreases in the amount of other constituents, according to the complexities of solubilities, plant uptake, and exchanges. Were one able to say for a given field condition to what fraction of the initial volume the irrigation water would be reduced while in the soil, an analysis made of a test sample boiled down to that extent would be informative. That, however, is not practical, but it is possible to anticipate, approximately at least, how much the sodium percentage can increase as a result of carbonate precipitation. This can be done by computing the percentage of sodium after deducting from Ca plus Mg the sum of HCO_3 and CO_3. This "possible percentage sodium" is an upper limiting value which can connote either complete safety as regards permeability or various degrees of hazard according to the extra water passed through the soil to prevent undue concentration.

The discussion presented in this paper is largely an outgrowth of observations of the effects of prolonged use of water in two of the world's oldest irrigation developments: one, in Egypt along the Nile; and the other, in Iraq along the Tigris and Euphrates. Data in addition to those presented here, but with some overlapping, have been reported elsewhere (4). Black alkali was found to be prevalent in the Nile Valley, whereas none was at any time observed along either the Tigris or the Euphrates. Under the latter rivers, however, the accumulation of salt in the land has been sufficient to account for a major decline in populations and for damage to a great civilization. In view of the long use of these waters, interest would have been attached to their composition under any condition, but with the findings on the occurrence and nonoccurrence of black alkali in the two regions it seemed important to assemble for review as many analyses of the irrigation waters as possible. The data showed, among other things, that residual sodium carbonate was always a constituent of the Nile water but never of the waters of the Tigris and Euphrates.

The analyses of the waters of the Nile presented in table 1 are recomputed from those assembled by Ball (1, p. 115). A good many analyses have been made of the waters of the Tigris, the Euphrates, and their tributaries, but few of these have been published. The analyses of the two rivers as of October 1920, representing a low water stage, are from Webster (12). The analyses of the Tigris for periods of high and low water are from a transcript of water analyses of Iraq assembled and presented to the writer by Vahe Sevian of the Irrigation Directorate of Iraq. The seasonal changes in the concentration of the waters of the Tigris and Euphrates are evidently somewhat similar, but prolonged series of complete analyses of the Euphrates have not been made. The flood season of the Nile occurs in late summer and fall from waters originating south of the equator, whereas in Iraq the flood season comes in spring from snow and rain in the area north toward, and in, Turkey.

In table 1 "residual Na_2CO_3" represents the amount of HCO_3-CO_3 remaining after deduction of the concentrations of Ca and Mg. Percentage sodium "found" is computed as Na × 100 divided by Na + Ca + Mg. Percent sodium "possible" is Na × 100 divided by Na + Ca + Mg − HCO_3 (the HCO_3 deduction not exceeding Ca + Mg).

TABLE 1

Waters of the Nile at Cairo and the Tigris and Euphrates near Bagdad*

SOURCE	YEARS	CATIONS			ANIONS			RESIDUAL Na_2CO_3	PERCENTAGE SODIUM	
		Ca	Mg	Na	HCO_3	SO_4	Cl		Found	Possible
		me./l.	*me./l.*	*me./l.*	*me./l.*	*me./l.*	*me./l.*	*me./l.*	%	
Flood:										
Nile—4 months	1906–36	0.64	0.57	0.50	1.44	0.16	0.14	0.23	32	100
Tigris—3 months	1925–28	2.39	0.85	0.38	2.75	0.49	0.39	0	10	44
Low:										
Nile—8 months	1906–36	0.87	0.72	2.04	3.03	0.23	0.46	1.44	55	100
Tigris—9 months	1925–28	2.78	1.64	0.71	3.56	0.94	0.63	0	14	45
Tigris, October	1920	3.93	1.99	0.44	3.00	1.81	1.55	0	7	13
Euphrates, October	1920	3.42	2.84	0.66	2.92	1.79	2.21	0	11	17

* Potassium, nitrate, and phosphate reported in the Nile analyses are omitted, as are 0.54 and 0.57 ml. of calcium reported as calcium silicate in the flood and low water, respectively. There was a corresponding amount of molecular silica. The silicate, according to Gracie *et al.* (5), precipitates in the Egyptian black-alkali soils a magnesium salt.

With the exception of the rather high concentrations of chloride found when the Tigris and Euphrates Rivers contained very little water in October 1920, all of the analyses reported in table 1 would be classed as excellent. By the usual standards, one would almost inevitably conclude that these waters should support a flourishing irrigation agriculture.

As regards the Tigris (and the Euphrates) this conclusion would undoubtedly have conformed with experience had the people through the centuries recognized the need of drainage to carry away the excess of salt. But there is no record of any ditch ever having been dug for this purpose in Iraq, a country where there is very little natural drainage except along river banks. It is only along river banks that many plants other than palms will do well or even survive. The major point to be made from the analyses of the Tigris (and Euphrates) waters is that the calcium and magnesium concentrations are so high relative to sodium in the initial waters (percentage sodium found) as well as after deduction of bicarbonate (percentage sodium possible) that any accumulation of salt would of necessity be classed as calcium salinity; that is, all the "possible percentage sodium" values are well below the 2:1 sodium-calcium ratios designated by Kelley (8) for the soil solution. There are many miles of abandoned irrigation canals in Iraq and millions of acres of once irrigated land that is now too saline for use. These lands need only drainage and leaching for reclamation.

The effects upon Egyptian soils of using Nile water are responsible for the present paper. Neither flood- nor low-stage Nile water contains as much as 60 per cent sodium. If the amount of calcium present as calcium silicate had been included in calculating the percentages of sodium, these would have been 22 and 49 per cent respectively. And yet, notwithstanding some past impressions about sodium percentages which were safe or unsafe, there is much low permeability in Nile soils and also there is much black alkali. Such occurrences become more understandable when residual sodium carbonate and the "possible" percentage sodium are computed. Residual sodium carbonate seems always to be a constituent, and in each case the "possible" percentage sodium is 100. A "possible" percentage sodium of 100 will always be found if residual Na_2CO_3 is present.

Characterization of the salts in river waters can be made with most assurance on the basis of a series of samples, or much better—particularly if flood waters are impounded in reservoirs—on the basis of means weighted for discharge. As an indication, nevertheless, of the trends among western river waters of the United States, a table of analysis reported by the U. S. Regional Salinity Laboratory (11) is reproduced here as table 2. Several of the original columns have been omitted and columns showing residual sodium carbonate and "percentage sodium possible" have been added.

As reported in table 2, none of these rivers were sampled more than once at any location, and from other data it is known that quite different waters are sometimes obtained at other stages and seasons. But in the results as tabulated, only five of the samples (two from Kings River) contained residual sodium carbonate. Also, no sample contained as much as 70 per cent of sodium. On the basis of "possible" percentage sodium, half of the samples had this much. It is thus to be observed that many waters like the Nile, that would be classed as safe on the basis of 60 or 70 per cent sodium, do have impermeability possibilities. On the other hand, the same calculation shows that other waters in the list could not produce soil solutions with enough sodium to cause impermeability.

The writer, at some time or other, has visited parts of each of the valleys served by the rivers of table 2. He knows that black alkali occurs in some of them and he believes it to be entirely absent from others, but he would not dare trust his memory for any assertion as to whether there is or is not a good correlation between the occurrence of residual sodium carbonate in the water supply and black alkali in the soil. As along the Nile, the formation of black alkali by use of a residual sodium carbonate water is directly contingent upon drainage conditions and whether the water has been used in enough excess to maintain calcium and magnesium in solution in substantial proportion. Some of the richest irrigation agriculture of the world is found on many of the lands served by the Nile. The finding of high "possible" percentage sodium values and the presence of residual sodium carbonate in some of the waters of table 2 constitute warnings that care must be exercised and that it is usually better to prepare drainage works while production is ample to pay for them than after the urgency is great.

TABLE 2

Chemical composition of some river waters used for irrigation in western United States

RIVER	Ca	Mg	Na	K	HCO_3+CO_3	Cl	SO_4	RESIDUAL Na_2CO_3	PERCENTAGE SODIUM	
									Found	Possible
	me./l.	*me./l.*	*me./l.*	*me./l.*	*me./l.*	*me./l.*	*me./l.*	*me./l.*		
Gila	3.59	1.99	11.27	—	3.88	9.95	3.26	—	67	87
Salt	2.28	1.30	8.09	—	2.71	8.58	0.84	—	69	90
Colorado	4.79	2.11	4.06	—	2.64	2.05	6.39	—	37	49
Kings	0.33	0.03	0.30	—	0.47	0.03	0.14	0.11	40	100
Kings	0.68	0.09	0.66	—	1.10	0.15	0.18	0.33	46	100
Owens	0.41	0.55	0.91	—	1.45	0.35	0.07	0.49	49	100
Sacramento	0.47	0.32	0.22	—	0.73	0.09	0.15	—	21	79
San Joaquin	1.94	1.47	3.22	—	2.65	3.90	0.27	—	49	81
South Platte	4.37	1.64	3.85	.13	3.96	1.45	4.05	—	37	61
South Platte	8.07	4.70	6.96	.41	4.02	1.44	15.04	—	35	43
Colorado	4.60	3.34	6.83	.12	3.42	5.71	4.55	—	49	60
Arkansas	7.18	3.49	3.47	.24	3.95	0.62	9.80	—	24	33
Poudre	0.62	0.22	0.19	.04	0.76	0.05	0.14	—	18	61
Payette	0.59	0.17	0.27	—	0.76	0.05	0.08	—	26	100
Boise	0.81	0.34	0.25	—	0.91	0.05	0.32	—	18	33
Rio Grande	1.86	0.70	0.83	—	1.77	0.14	1.50	—	24	51
Rio Grande	2.84	1.05	3.00	—	2.67	1.10	3.20	—	44	71
Pecos	21.70	8.10	12.70	—	4.20	38.10	9.00	—	27	33
Pecos	7.63	6.78	32.02	—	1.70	23.33	12.44	—	69	71
Rogue	0.54	0.26	0.33	.02	0.85	0.25	0.00	0.05	29	100
Sevier	3.30	7.50	15.20	.03	4.20	14.0	8.30	—	58	70
Columbia	0.90	0.39	0.19	—	1.26	0.07	0.21	—	13	86
Yakima	1.14	0.73	0.73	.08	2.23	0.20	0.31	0.36	27	100
Big Horn	3.08	1.19	1.96	—	2.58	0.76	3.17	—	31	54

In a water-quality survey (2) of the San Joaquin Valley, 444 samples were collected from wells and streams. By present calculation, about half of these samples contained residual sodium carbonate. In many others there was enough bicarbonate to move the water from "safe" to "uncertain" brackets when "possible" percentage sodium was calculated.

The writer is obligated to R. Earl Storie, in charge of soil survey for the University of California, for his cooperation in a test of the relation of residual sodium carbonate in San Joaquin Valley water supplies to the occurrence of black alkali in the soils irrigated. To make this test, each of the sample locations shown on the series of 28 twelve-township quadrangle maps (2) was marked by the writer to show the occurrence, or nonoccurrence, of residual sodium carbonate in the water supply. When the water contained residual sodium carbonate, the location was marked with one to five dashes to designate a class concentration. Professor Storie compared the occurrence of residual sodium carbonate in these water supplies with the occurrence of black alkali on his soil maps of the same region. It was, of course, mutually understood that some of the wells recorded by the writer were municipal or industrial, some had undoubtedly been abandoned, some replaced, some were not necessarily representative of the water supplies generally used for irrigation, and some districts were missed entirely or only incompletely sampled. It was further understood that there was undoubtedly much black alkali in parts of the San Joaquin Valley when men started to irrigate. Professor Storie's comments on the results of his study included the following: "In general I find nothing in conflict with the alkali condition shown on our soil maps; in fact, as mentioned previously, your red dashes check very closely with the black alkali soils of the valley."

Quadrangles 24 and 25 of the publication cited include the bed of old Tulare Lake and the region immediately to the east. The agriculture in this area is served almost entirely by wells (usually 1,000 or more feet deep). The Kings River contains a little residual sodium carbonate, and in time of flood in the past it has overflowed into the old lake bed. Of the 32 samples which were collected (mostly in 1929 and 1930) from wells in these two quadrangles, all but one contained residual sodium carbonate and the concentration usually was substantial. Professor Storie characterizes quadrangle 24 as "black-alkali soils" and quadrangle 25 (just to the east) as having "many black-alkali soils." Old analyses of Tulare Lake waters, two in 1880 and one in 1889, showed respectively 9.11, 9.86, and 30.34 me./l. of residual Na_2CO_3. In other words, at least some of these lake-bottom soils have probably been laid down in, and subsequently subjected to, Na_2CO_3 waters prior to irrigation activities.

Among the deep wells along the axis of the San Joaquin Valley, a number were found to produce water containing less sulfate than the present-day streams that flow into the valley. These waters had high sodium percentages and much bicarbonate, and some of them marsh gas, all of which contributed to the idea (3) that sulfate originally present had undergone anaerobic decomposition. Such anaerobic activity has been variously described by equations of the following nature: $CaSO_4 + CH_4 = CaCO_3 + H_2S + H_2O$, and $CaSO_4 + 2C = CaS + 2CO_2$. This subject is mentioned for two reasons: first, because the equations show that the anaerobic activity can remove calcium from solution by converting fairly soluble $CaSO_4$ into the nearly insoluble $CaCO_3$, and thereby increase sodium percentages; and second, because Gracie *et al.* (5) have regarded anaerobic sulfate-reducing activity as being responsible for black-alkali formation in Nile lands. They considered CO_3 to be developed by the action on the soil organic matter of the oxygen liberated from SO_4 by anaerobic processes. In this anaerobic process each SO_4 ion can produce one CO_3 ion and this in turn can precipitate one Ca ion. For the activity to proceed through the formation of

Na-clay, it is necessary, therefore, that sufficient SO_4 (and organic matter) be present in the system to develop the CO_3 necessary to precipitate the Ca and Mg of the soil solution, as well as the Ca and Mg to be displaced from the exchange complex of the soil. In the Nile Valley, the SiO_3 ion may take care of the Mg, but the water does not carry enough SO_4 to form sufficient CO_3 to precipitate the Ca. At flood and low stages of the Nile there are 0.16 and 0.23 me./l. of SO_4 respectively and 0.64 and 0.87 me./l. of Ca; in other words, Ca is always three or four times as concentrated as SO_4. Anaerobic sulfate decomposition could thus dispose of only about one third of the soluble Ca as $CaCO_3$. If all of the SO_4 were used up in the formation of CO_3 and this were all precipitated as $CaCO_3$, enough Ca would still remain in solution to block the formation of Na-clay. If the sulfate utilized were that of the gypsum found nearby, there could still be no net gain, since that Ca would merely be transformed from gypsum to lime. To regard the matter from the viewpoint of the present paper, an ample supply of $HCO_3 + CO_3$ is already contained in Nile water to precipitate the water's Ca and Mg and to leave additional carbonate to be associated with sodium to increase the pH and to contribute, as well, to the precipitation of exchangeable Ca and Mg of the clay as these ions are replaced by Na. There is no reason to doubt that sulfate decomposition, under some circumstances, might hasten and contribute to black-alkali formation, but in the instance of the Nile lands it is not necessary to postulate sulfate decomposition to account for the formation of black alkali.

The fact that the investigators in Egypt (5) reported networks of gypsum in soils near those with black alkali has a rather significant implication. The Nile flood water contains 0.16 me./l. SO_4. For this concentration of sulfate to start crystalizing out in a pure solution, the volume would have to be reduced to 175th of the initial. Actually, in soils, calcium sulfate has been observed to remain in solution at double its theoretical solubility of 28 me./l. The conclusion to be drawn is that for the formation of gypsum, Nile water had to undergo approximately a 200-fold volume reduction. Such may not be at all unusual in many irrigated soils with high water tables or impervious layers, and it serves to justify consideration of water quality in terms of concentrates that have volumes which are only a small fraction of the initial water.

The mixed conditions of highly fertile soils and alkali soils under the Nile illustrate that the use of an irrigation water that yields sodium carbonate upon evaporation does not always lead to black-alkali formation. Soils that contain some black alkali but which are not yet entirely impervious are often reclaimed without use of soil amendments by providing drainage and then leaching with water from the same source as that which produced the condition. This has been accomplished in Egypt, and Kelley and Brown (7) have demonstrated the feasibility of such reclamation in the alkali soils near Fresno, California. After the land at Fresno was drained, it was leached with water that was probably not very different from waters of the general region, some of which contain considerable residual sodium carbonate. Use of soil amendments, however, hastened reclamation; sulfur was especially effective in that calcareous soil.

In keeping with what one would expect from the analyses of the Tigris and Euphrates, the soils which have been served by these waters are free from black alkali. Data by Webster (13) and the results obtained from small test plots support the conclusion to be drawn from the water analyses that calcium saline soils are represented and have been responsible for wholesale abandonment.

SUMMARY

Black alkali occurs frequently in soils irrigated by the Nile in Egypt. Analyses show that Nile water consistently contains residual sodium carbonate, that is, more HCO_3 and CO_3 than Ca and Mg. In his early investigations, Hilgard associated the occurrence of black alkali in soils with sodium carbonate in water supplies, and that relationship might again be used to advantage in judging the properties of irrigation waters. Half of a group of 444 water samples from the San Joaquin Valley of California have been found to contain residual Na_2CO_3.

Soils of Iraq are irrigated from the Tigris and Euphrates. These waters contain much more calcium and magnesium than carbonate and bicarbonate and also more calcium and magnesium than sodium, and no black alkali has ever been found. Although these rivers contain only a little salt, millions of acres of land are now too saline for crops and great irrigation canals lie abandoned because of absence of drainage.

When lands are irrigated with water containing more than twice as much sodium as calcium and magnesium, permeability is likely to be impaired. This relation in water supplies is customarily expressed as percentage sodium. As discussed in this paper, water with a low initial percentage sodium may give rise to a high-sodium soil solution by reason of calcium carbonate precipitation, whereas the percentage sodium of other waters with little $CO_3 + HCO_3$ will change little during evaporation. That the magnitude of the possible change, in the soil, of percentage sodium may be taken into account in appraising water quality, it is suggested that both the percentage sodium "found" and the percentage sodium "possible," as well as residual sodium carbonate, might be profitably reported in conjunction with analyses of irrigation waters.

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EFFECT OF GASEOUS PHASE ON WATER-STABLE SYNTHETIC AGGREGATES[1]

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An investigation by the author to determine the effect of particle-size of minerals on aggregation has drawn attention to an interesting phenomenon—an anomalous role of the gaseous phase in water-stable aggregates. The well-known disruptive influence of air inside the aggregates when these are suddenly wetted by water has been recognized by many. In this paper the evidence obtained from dispersion measurements with synthetic hydrogen aggregates from expanding and nonexpanding crystal-lattice types of clay minerals suggests that the gaseous phase not only has a disruptive influence but also a protective effect and aids in maintaining the stability of smaller aggregates. The results of the experiment also suggest a standard method in wetting dry aggregates for their measurement of size distribution in water.

EXPERIMENTAL PROCEDURE

To investigate the effect of the gaseous phase on water-stable aggregates, the clay fractions were separated from Hesperia sandy loam and kaolinite. The sandy loam was collected from the cultivated, 8-inch surface of the plots studied by Bodman and Mazurak (4) near Shafter, California. The light grayish brown micaceous soil is a recent alluvial material derived from granitic rocks. Although distinct natural horizons appear to be lacking in the profile, the deeper part may be calcareous. The soil was given the same pretreatment as for ultimate analysis. This treatment consisted of digesting with H_2O_2, washing with HCl and water, and adding $(NaPO_3)_6$ with overnight shaking in a reciprocal shaker. The particles $<1.15\mu$ were separated by gravity sedimentation, and a portion of the suspension of particles $<1.15\mu$ was centrifuged in a Sharples supercentrifuge to obtain particles $<0.15\mu$.

The kaolinite, from South Carolina, was crushed with a rubber-tipped pestle in a mortar and was dry-ground in a ball-mill for 24 hours. It was then dispersed in water with $(NaPO_3)_6$, and particles $<1.15\mu$ were separated by gravity sedimentation. Of the particles $<1.15\mu$, 12 per cent were 1.15–0.58μ, 26 per cent 0.58–0.29μ, 23 per cent 0.29–0.15μ, and 39 per cent $<0.15\mu$.

The suspensions of kaolinitic particles $<1.15\mu$ and particles $<0.15\mu$ from

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[3] Temporarily withdrawn; resubmitted September 10, 1949.

Hesperia sandy loam were electrodialyzed. They were then slowly dried to induce aggregation. In synthesizing aggregates from suspensions, the particles were given a good opportunity to come in contact with one another during drying. Thus, the suspensions were slightly stirred to reduce as much as possible the gravity settling of particles, frictional forces, and air bubbles. The material was allowed to dry slowly for 2 or 3 weeks without being manipulated in the thick consistency state. Preliminary experiments with drying methods showed that, of the many ways tried, placing the beaker with the suspension on top of an electric drying-oven or steambath gave the largest aggregates. This procedure was followed, therefore, in most cases. In special experiments, however, suspensions were dried over concentrated sulfuric acid in a desiccator evacuated to the boiling point of water.

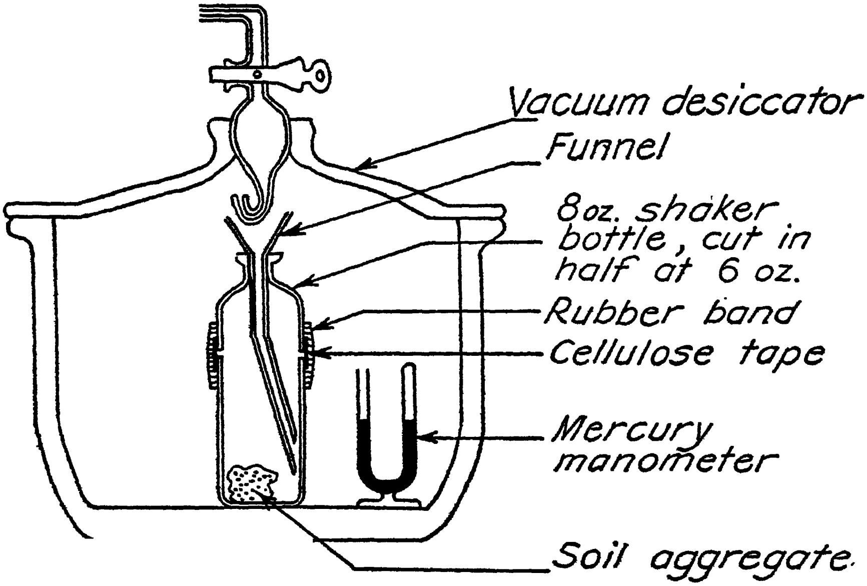

FIG. 1. VACUUM DESICCATOR WITH A SINGLE DRY AGGREGATE PRIOR TO WETTING WITH WATER

Synthetic aggregates so formed were prepared for analysis by wetting under vacuum in the apparatus shown in figure 1. The bottle containing a single aggregate was left overnight in an evacuated desiccator. Water was then admitted slowly under partial vacuum through the glass-tube intake. At first, the aggregate was only partly wetted, to allow escape of entrapped air and also to prevent vigorous boiling of the water. Later, more water was added until the aggregate was immersed in 5½ ounces. The shaker-bottle was then placed in a reciprocal shaker. Four samples were shaken for 2-, 20-, 200- and 2,000-minutes, respectively, to produce varying degrees of dispersion. In all cases, the total time of immersion was approximately 2,200 minutes.

In addition to this standard procedure of wetting aggregates, three additional methods of wetting kaolinitic aggregates in the shaker-bottle were used: (*a*) aggregate flooded with water; (*b*) aggregate in a shaker-bottle flooded with water and the bottle placed in a desiccator, which was immediately evacuated to the boiling point of water; and (*c*) aggregate in a shaker-bottle left overnight in a desiccator under partial vacuum, CO_2 slowly admitted through the intake until atmospheric pressure was reached, desiccator lid removed, aggregate flooded with water, and the bottle stoppered.

Aggregates containing particles $<0.15\mu$ from Hesperia sandy loam were wetted in the following manner: In addition to the standard procedure of wetting aggregates already described, a set of wetting treatments was obtained by flooding air-dried aggregates with water. In a second set of wetting treatments the air-dried aggregate under partial vacuum was wetted with CO_2-saturated water. In a third, fourth, and fifth set the suspensions were dried over concentrated sulfuric acid under partial vacuum at the boiling point of the suspension. These three sets were then wetted in the following ways: In the third set of samples water was added without admission of air, the gaseous phase consisting of residual air plus any water vapor left in the partly evacuated desiccator. In the fourth set of samples air was admitted into the desiccator and the dry aggregates were left in the open for 2 weeks; then the desiccator with each dry aggregate in a shaker-bottle was evacuated, and the aggregate was left in partial vacuum overnight; and finally, the aggregate was wetted under partial vacuum. In the fifth set CO_2 was admitted slowly into the partly evacuated desiccator until its pressure equaled that of the atmosphere, and then the aggregate was flooded. The condition during drying of suspension, the treatment of aggregates prior to wetting, and the wetting condition are summarized in table 2.

The size distribution of aggregates in water was made by a combination of methods: wet-sieving ($>590\mu$), elutriation ($590 > 18.5\mu$), gravity sedimentation ($18.5 > 2.31\mu$), and centrifugation ($1.15 > 0.15\mu$). The size class-intervals used in the analysis are shown in figures 2 and 3 by the graduations on the abscissa scale which shows equal logarithmic intervals having limits equal to 2 over the range $9{,}400\mu$ to 0.15μ.

In expressing the results from aggregate analysis the summation curve is used without stressing any particular aggregate size. To permit comparisons of treatments with numerical values, the area under the C.C. (cumulative weight percentage curve) is calculated and related to the G.M. (geometric mean size). The G.M. has a physical dimension of length. By use of the standard deviation and the shape of particle, Hatch and Choate (10) have related the G.M. of particles to the surface area. This relationship gives more significance to the use of G.M. in aggregate analysis, since structural phenomena involve surfaces. The G.M. may be obtained from the usual method by the use of logarithm (13) or by the following short-cut method. The G.M. is the anti-logarithm of an average of logarithms, thus, the area under the C.C. (see fig. 2) to the right of G.M. is equal to the area to the left of G.M. and above the curve. Expressing this relationship mathematically:

$$\sum_{\substack{\text{Per cent less than the}\\ \text{smallest diameter}}}^{\substack{\text{Per cent less than}\\ \text{the largest diameter}}} (\text{summation percentage})(\log_{10} 2)$$

$$\begin{pmatrix}\log_{10}\text{ upper} & - & \log_{10}\text{ geometric}\\ \text{diameter, }\mu & & \text{mean, }\mu\end{pmatrix}(100)$$

Solving for G.M., μ:

$$\text{G.M.} = \frac{\text{Upper diameter, }\mu}{2\ \exp.\left(\dfrac{\Sigma\text{ Cumulative percentages}}{100}\right)}$$

A correction of $\frac{1}{2}$ log 2 for the class-interval is made, making the equation equal to:

$$\text{G.M.} = \frac{\text{Upper diameter, }\mu}{2\ \exp.\left(\dfrac{\Sigma\text{ Cumulative percentage} - 50}{100}\right)}$$

RESULTS

The first evidence for the effect of gaseous phase on water-stable aggregates was deduced from an investigation on the effect of particle size of minerals on synthetic water-stable, hydrogen aggregates which will be reported in a future publication. It is briefly summarized here. As the particle sizes from Hesperia sandy loam decreased, the G.M.'s of aggregates increased, as was expected for the 2-, 20-, 200-, and 2,000-minute shaking, except for particles $<0.15\mu$ after 2- and 20-minute shaking. The less aggregation of particles $<0.15\mu$ in contrast to aggregates containing particles 0.29–0.15μ was attributed to failure to remove the air remaining in the dry aggregates containing particles $<0.15\mu$ after partial evacuation. This was suggested by the similarity in behavior between dry aggregates wetted under partial vacuum and those immersed in water under atmospheric conditions. The similarity was in the explosive action in the aggregates as evidence by popping and cracking, by small aggregates flying off the larger piece in the water, and, frequently, by air bubbles shooting from the water surfaces. The swelling property, which was absent for separates $>0.15\mu$, was thought not to be the primary cause of disaggregation, because the process occurred in a few seconds. It is not meant to imply that swelling is not important, for swelling would result in differential stresses and strains in the aggregates, causing them to disintegrate. Furthermore, if the adsorbed and entrapped air aided in disaggregation, the greater water-stablity of aggregates containing particles $<0.15\mu$ than those containing particles 0.29–0.15μ was not readily explainable.

Aggregates containing particles $<1.15\mu$ from kaolinite

With the background of the above experimental evidence from aggregates containing separates obtained from Hesperia sandy loam, kaolinite was used to test the validity of the hypothesis of the effect of air on aggregation. The results of different wetting methods mentioned in the experimental procedure are given

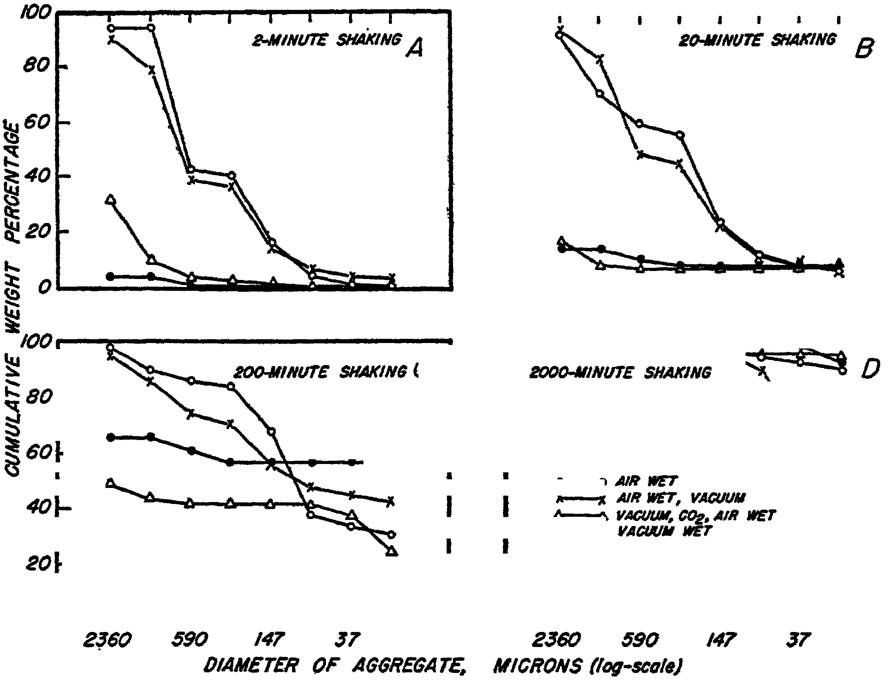

FIG. 2. CUMULATIVE CURVES FOR AGGREGATES CONTAINING PARTICLES <1.15 μ OBTAINED FROM KAOLINITE, AFTER DIFFERENT WETTING TREATMENTS AND SHAKEN IN WATER FOR 2-, 20-, 200-, AND 2,000-MINUTES

TABLE 1

Geometric mean size and water-stability of aggregates formed from <1.15μ particles of hydrogen kaolinite, as affected by method of wetting

TREATMENT OF AIR-DRIED AGGREGATES		GEOMETRIC MEAN				
		Aggregate analysis				Ultimate analysis on the basis of < 18.5μ particles
Prior to wetting	After wetting	2-min. shaking	20-min. shaking	200-min. shaking	2,000-min. shaking	
(air wet)*		μ	μ	μ	μ	μ
none	none	445	351	86	15	13
(air wet, vacuum)						
none	vacuum	527	368	98	27	13
(vacuum wet)						
vacuum	none	>3500	1670	122	14	13
(vacuum, CO₂, air wet)						
vacuum CO₂	none	>3500	3340	503	15	13

* Phrase in parentheses identifies the curves in figure 2.

in figure 2. The G.M.'s of aggregates are given in table 1, in which the phrase in parenthesis in the first column identifies the C.C.'s in figure 2. The G.M.'s are slightly higher than the true values, for the calculation does not include sizes below 18.5μ but assumes that the particles and aggregates $<18.5\mu$ are in the size class 18.5–9.25μ. Aggregate analysis was made on sizes below 18.5μ, but because of flocculation of particles and aggregates in the sedimentation method, the measurements were not included. To enable one to make comparisons on the degree of dispersion, the G.M. of ultimate particles is given on the basis of $<18.5\mu$. The fact is, however, that the particles used were $<1.15\mu$.

The partial evacuation of air from dry kaolinitic aggregates and the wetting under vacuum (vacuum wet curve) did not disperse the aggregates, as shown by the C.C.'s in figure 2A and the G.M.'s for the 2-minute shaking in table 1. Replacement of air by a soluble gas in the dry aggregate and flooding with water at atmospheric pressure (vacuum, CO_2, air wet curve) gave results comparable with the vacuum method of wetting (figs. 2-A and -B). In figure 2-A the 2-minute shaking C.C. shows a very slight dispersion of coarse aggregates containing CO_2 when immersed in water in comparison to the vacuum wet method, suggesting that possibly CO_2 did have a slight dispersing effect. No such effect of CO_2 is evident for the 20-minute shaking C.C. in figure 2-B. In the 200-minute shaking the aggregates containing CO_2 gave less dispersion than those wetted under partial vacuum. Apparently, CO_2 does contribute to the stability of kaolinitic aggregates. The slight dispersing effect for the 2-minute shaking is attributed to CO_2 in the large pores, whereas the stability of aggregates is attributed to CO_2 in the very small pores. Partial vacuum method of wetting aggregates gave a higher G.M. and a lower dispersion curve for the 200-minute shaking than those flooded in water under atmospheric conditions (air-wet and air-wet vacuum curves).

The slopes of C.C.'s for aggregates containing CO_2 (vacuum, CO_2, air-wet curves) and those wetted in partial vacuum show that the aggregates wore down with increase of shaking time. Microscopic examination of aggregates after shaking in water showed them to be smooth and ovoid, which suggests attrition. A bimodal distribution of aggregate sizes $>2{,}360\mu$ and $<18.5\mu$ is present with very few aggregates between these sizes. Aggregates with air in the interior and immersed in water, however, showed variation in size distribution of aggregates from 2 to 200 minutes of shaking. Attrition of the aggregates after shaking in water is brought out clearly when the C.C.'s for aggregates at different shaking times are plotted separately for each treatment. The curves have approximately identical slopes, but are displaced toward the smaller aggregate sizes.

With the 2,000-minute shaking, the aggregates of all treatments abraded to sizes $<18.5\mu$, with the exception of the air-wet, partial vacuum treatment. The fact that the C.C. for this exception showed aggregation of particles of 150μ may be attributed to the short period during which the system was subjected to partial vacuum, namely, 200 hours in contrast to 2,000 hours for all others. Another plausible explanation is that the remaining entrapped air in the aggregates may be responsible for their stability.

Aggregates containing particles $<0.15\mu$ from Hesperia sandy loam

Dry hydrogen-aggregates containing particles $<1.15\mu$ or $<0.15\mu$ from Hesperia sandy loam behaved similarly to each other when the aggregates were wetted under partial vacuum. Since the hydrogen aggregates containing particles $>0.15\mu$ did not show the explosive action during wetting under partial vacuum, the cause of shattering was associated with particles $<0.15\mu$, which amounted to 70 per cent of $<1.15\mu$ particles. Use of aggregates containing particles $<0.15\mu$ simplifies the interpretation of results. The wetting treatments of aggregates, given in experimental section, are summarized in table 2, together with the G.M.'s of aggregates and their stability in water. The C.C.'s for aggregates are shown in figure 3.

The G.M.'s in table 2 are arranged in a descending order of values for the 2-minute shaking. The relative position for each treatment holds for the 20-minute shaking. The aggregates obtained from suspensions dried in partial vacuum and then wetted gave higher G.M. of aggregates than those from suspensions dried in air. In the partial vacuum set (treatment 1) the aggregates probably have only water vapor with very little air in the pores to obstruct the particles from coming into greater contact with one another during the drying of suspension. These aggregates when wetted under partial vacuum showed the least dispersion, because the air phase was absent in the system. Dry aggregates with the pores filled with CO_2 showed the second highest G.M., while those filled with air and then partly evacuated were the lowest in G.M. after the aggregates were wetted. The reason for the latter's having the lowest G.M. of aggregates is that not all the air in very fine pores and surfaces of aggregates can be removed by a single evacuation (16). On the other hand, the dry aggregates obtained from suspensions dried in air, as much air as possible being evacuated before wetting, showed a higher G.M. than those without any vacuum treatment. If a gas were expanding in the interior of the aggregate, even though the aggregate is in partial vacuum, while being wetted, the process should greatly disperse the aggregate. This is shown by the set in which the partly evacuated aggregate was wetted by water saturated with CO_2 (treatment 6).

In the 2,000-minute shaking, the aggregates obtained from suspensions dried in air show the *least* dispersion in contrast to those from suspensions dried in partial vacuum. The property of adsorbed air is given as the cause of the stability of aggregates. The presence of air in the aggregate probably prevents the water from penetrating the aggregate. In table 2 the G.M. of aggregates from suspensions dried in air gave higher values in two out of three cases than those for suspensions dried in partial vacuum series. The latter, owing to less air present in the aggregate, yielded a higher dispersion in two out of three cases, in spite of the fact that their aggregates had the largest size-distribution initially. The aggregates formed from vacuum-dried suspensions and vacuum-wetted without admission of air, gave the lowest G.M. out of six treatments. In table 2 the order of descending G.M. of aggregates for the 2,000-minute shaking after different wetting treatments is as follows: $4 > 6 > 2 > 5 > 3 > 1$.

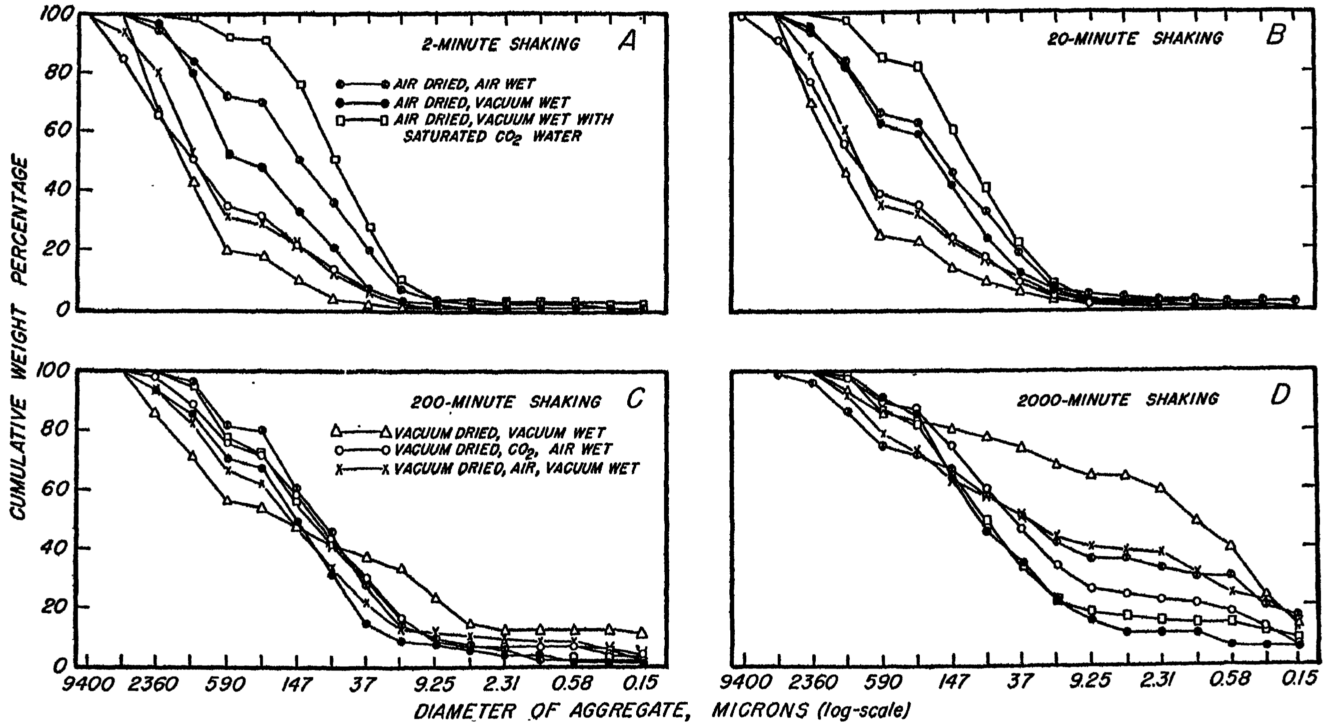

FIG. 3. CUMULATIVE CURVES FOR AGGREGATES CONTAINING PARTICLES <0.15 μ OBTAINED FROM HESPERIA SANDY LOAM, AFTER DIFFERENT WETTING TREATMENTS AND SHAKEN IN WATER FOR 2-, 20-, 200-, AND 2,000-MINUTES

In the 200-minute shaking the effect of treatments are not too well-defined for most cases. The tendency is for the treatments to approach that for 2,000-minute shaking.

The separate plotting of the C.C.'s for aggregates of the same treatment but different shaking times suggests that shaking water-suspended aggregates in a container is merely an abrasion process. Experiments with kaolinitic aggregates lead to the same conclusion. The size distribution of aggregates after the dry aggregates have been wetted is largely determined by the method of wetting, as shown in figure 3A. The 2- and 20-minute shakings did not yield very many particles or aggregates below 9.25μ. In figure 3C the 200-minute shaking shows an appreciable amount of fine material for the aggregates from suspensions dried under partial vacuum and wetted without admission of any gas.

TABLE 2

Geometric mean size and water-stability of aggregates formed from $<0.15\mu$ particles of Hesperia hydrogen clay as affected by method of wetting

TREATMENT NUMBER	TREATMENT OF DRY AGGREGATES			GEOMETRIC MEAN			
	Condition during drying of suspension	Prior to wetting	Wetting condition	2-min. shaking	20-min. shaking	200-min. shaking	2,000-min. shaking
	(vacuum dried, vacuum wet)*			μ	μ	μ	μ
1	vacuum	none	vacuum	1,040	765	82.1	3.72
	(vacuum dried, CO_2, air wet)						
2	vacuum	CO_2 admitted to ca. 1 atmos.	1 atmos. of CO_2	740	556	84.4	22.8
	(vacuum dried, air, vacuum wet)						
3	vacuum	air admitted, evacuated	vacuum	645	468	116	16.2
	(air dried, vacuum wet)						
4	1 atmos. of air	evacuated	vacuum	300	216	146	48.8
	(air dried, air wet)						
5	1 atmos. of air	none	1 atmos.	148	168	78.7	18.5
	(air dried, vacuum wet with sat'd CO_2 water)						
6	1 atmos. of air	evacuated	vacuum with CO_2-sat'd water admitted	68	100	82.6	41.3

* Phrase in the parentheses identifies the curves in figure 3.

As with the results of the C.C.'s for kaolinitic aggregates, no consistent, simple mathematical relationships exist between G.M. and increase in shaking time for aggregates from Hesperia of $<0.15\mu$ particles. Stability of aggregates is readily apparent from table 2. The aggregates from suspensions dried in partial vacuum are less resistant to change in G.M. of aggregates on shaking than are those from suspensions dried in air. At the beginning of shaking, however, larger aggregates are present in the former than in the latter. It should be noted that once the wetting had dispersed the aggregates, as in treatment 6, the CO_2 gas aided in maintaining the stability of aggregates (table 2).

In table 2, treatment 6, difficulty was experienced in getting the CO_2-saturated water down the stem of the funnel because of sudden expansion of CO_2 with the formation of bubbles. To obtain consistent results, the stem of the funnel should be sufficiently wide to prevent the formation of bubbles.

The different methods of wetting dry aggregates shown in tables 1 and 2 produced aggregates of various sizes, shapes, and forms. No quantitative measurements were made on the shape and form or on the quality of these aggregates. The aggregates from suspensions dried in vacuum formed definitely more platy and gelatinous aggregates after wetting than did those from suspensions dried in air. The gaseous phase is undoubtedly a factor to be considered in the shape and type of structural forms.

DISCUSSION

The disintegration of large aggregates into smaller sizes under natural conditions was recorded in the literature in 1650 (15). This well-known fact is utilized in the field by allowing the soil to remain fallow. With alternate drying-wetting or with freezing-thawing, which is essentially a drying-wetting process, or with both, smaller aggregates are produced (3). The wetting-drying phenomenon is an important process in irrigated regions, for a dry soil suddenly receives large quantities of water. Not many quantitative data have been published on the effect of irrigation on the aggregate size-distribution. The effects of a drying-wetting cycle on a soil in the field probably depend on the method of wetting more than upon the mere repetition of drying and wetting of the soil, for the effect of the process appears to be largely dependent on the gaseous phase in the aggregate. For example, a clod of Hesperia sandy loam was alternately wetted with water by capillary action and air-dried for 20 cycles. The clod remained virtually the same size, but when the dry clod was flooded with water, it immediately slaked down.

The gaseous phase, a neglected factor in structural study, also appears to be closely related to the wettability of soils. Soils with a high content of iron or organic matter or air-dried pulverized soils are difficult to wet. Numerous German investigators (9) have associated the unwettability of such soils with adsorbed air. Wettability of soils was given considerable attention in Europe a few decades ago. Ammon, cited by Giesecke (9), gave the following figures on the adsorption of carbon dioxide [data for O_2, N_2, NH_3, and other gases are also given in this reference] by 100 ml. of iron hydroxide, humus, gypsum, and kaolin as 5,726, 930, 210.6, and 8.96 ml., respectively. These figures are of particular interest here, for the replacement of air by carbon dioxide in the dry synthetic aggregates followed by immersion in water had very little dispersive effect on the aggregates. It will also be recalled that entrapped or adsorbed air aided in maintaining the stability of small aggregates. These facts bring to mind the possible additional functions of organic matter, iron hydroxide, and microorganisms in soil structure phenomena. Concerning aggregates containing organic matter or iron hydroxide intimately mixed with a soil mineral, the question arises as to how much the stability is the result of cementing materials and how much is due to the air, carbon dioxide gas, or other gases adsorbed on these surfaces. Thus, it appears that the coating of the primary minerals and of elementary structural forms becomes important in interpreting the physical properties of soil. Tiulin's work (18) stresses this fundamental aspect of soil structure. Similarly, many investigators (1, 2, 7, 8, 12, 16) have shown the effect of gaseous phase on soil properties.

The phrase "effect of entrapped and adsorbed air" was used many times in this article. The part played by each in disaggregation was not studied quantitatively, as this required a new set of experimental conditions. Furthermore, the composition of the gaseous phase, of which water vapor is an important constituent, has not been rigidly controlled in these experiments. The experiments with CO_2 gas suggest that the presence of water vapor will have the same effects on aggregates. The procedure used, however, possibly gave the minimum amount of water vapor encountered in soils under atmospheric conditions.

When an air-dried aggregate is immersed in water, many phenomena that are important in determining the size distribution of aggregates occur. The entrapped air is pushed inside the aggregate, and because of the insolubility of air, it is compressed by the capillary forces of water. The result is that the aggregates shatter. This explanation was confirmed experimentally by failure of the kaolinitic aggregates to shatter when the dry aggregates under partial vacuum were wetted by water. Moreover, Henin (11) obtained greater dispersion of dry aggregates when he wetted them at 3 atmospheres than at 1. The solubility of gases during wetting of dry aggregates is important in determining the aggregate-size distribution. The CO_2 was chosen to be present in the dry aggregates, rather than air or water vapor, to show the effect of solubility of gases in water during the wetting process. The CO_2, being soluble in water, would dissolve when the aggregate was wetted by water, and hence the explosive action should be absent. The increase of pressure of the CO_2 gas by the water's moving into the aggregate would dissolve more gas, according to Henry's law, thus further lessening the explosive action. A concentration gradient of the dissolved gas is probably established between the interior and the exterior of the aggregate. Escaping bubbles were observed coming from the aggregates containing CO_2 when they were flooded with water.

The second phenomenon which is thought to occur, simultaneously with the first, during the wetting of a dry aggregate is that the water-film displaces surface-adsorbed air and compresses the air into the aggregate. Sobolev and Chapek (17) have measured these two types of air and believe that the adsorbed air is more important than the entrapped air. This is rational, for we know that the adsorbed air is held comparatively rigidly to the surface. Its volume is probably small as compared to the released volume of gas, the expansion of which would tend to decrease the temperature inside the aggregate during the wetting process. This tendency is more than offset by the heat of wetting. The net effect is that of further increase in the gas pressure by the expansion of gas in the interior of the aggregate. Thus, it is quite evident that the nature of the adsorbents and the rate of wetting are important in determining the size distribution of aggregates.

As to the nature of adsorbent, which would indicate the amount of adsorbed air present during wetting of dry aggregates, a hydrogen kaolinitic aggregate formed from particles $<0.15\mu$ (obtained without ball-mill grinding) wetted under partial vacuum and shaken for 2 minutes in water gave a G.M. of aggregate of $>10{,}000\mu$. On the other hand, hydrogen aggregate from Hesperia of $<0.15\mu$ particles with treatment similar to that of kaolinite had a G.M. of 300μ. The particles in the two types of clay mineral are not likely to have the same size distribution, and this, together with differences in the nature of surfaces, would affect the quality of aggregates. The pore size, for instance, of kaolinitic aggregate was probably larger, as evidenced by the soft, dry aggregates, than in the Hesperia, which had hard aggregates. Hence the partial evacuation may have been more complete in kaolinite than in Hesperia aggregates. The importance of pore size, hence the permeability of aggregates, in shattering aggregates during wetting is quite apparent. Further evidence that permeability of aggregate is important in determining the size and stability of aggregates is based on the fact that when one symmetry concentration of Na^+ was added to electrodialyzed suspension of particles $<0.15\mu$ obtained from Hesperia, followed by drying in air, and then wetting under partial vacuum, the sodium aggregates did not show the explosive action but, instead, showed slow slaking. This suggests that the effective pore size in the sodium aggregate must be too small for the entrance of water, and that the only way for it to enter the aggregate was by gradual removal of the surface layers of aggregate. Thus it was reasoned that the stability of hydrogen aggregates containing particles $<0.15\mu$ was probably due to failure of water to wet the solid. In addition to the small effective pore-size, the air remaining inside the comparatively larger pores in the aggregate developed sufficient pressure to oppose the force of adhesion of water to the solid. For the particles to disperse in water, it would be necessary for the water to wet the particles. The exact mechanism by which the air promotes greater stability of aggregates cannot be known without further experimental work.

SUMMARY

Experimental data are presented for hydrogen aggregates synthesized from kaolinite particles $<1.15\mu$ and from particles $<0.15\mu$ of an expanding lattice clay separated from Hesperia sandy loam. The latter clay contained some hydrous mica.

A method of wetting dry aggregates under partial vacuum is described. Its use is suggested as a method for wetting natural aggregates for aggregate analysis in water. Sieves, elutriator, gravity- and centrifugal-sedimentation methods were used to obtain aggregate sizes over the range 9,400 to 0.15μ and finer, size-

class limits spaced at intervals corresponding to a geometric progression with the common factor 2.

Aggregation is expressed by geometric mean size of aggregates, which is inversely related to the surface area. The larger the geometric mean, the greater is the aggregation. The geometric mean size is used with the curves of cumulative weight percentage of aggregates in interpreting the data.

The size of synthetic aggregates in water depended on the method of wetting and on the composition of gas inside the aggregate at the time of wetting. Dry aggregates wetted under partial vacuum gave a larger geometric mean of wet aggregates than did aggregates immersed in water under normal atmospheric conditions. The replacement of air by CO_2 in the aggregates and subsequent immersion in water under atmospheric pressure gave comparable results to that of the partial vacuum wet technique. Expansion of gas in the aggregates caused the aggregates to disintegrate.

The stability of aggregates in water was determined from the size distribution of aggregates at various shaking times, namely, 2-, 20-, 200-, and 2,000-minutes. The stability of aggregates, that is, the resistance to change in geometric mean size of aggregates on shaking, was less in the aggregates wetted under partial vacuum than in those wetted in air. The relatively insoluble gas (air) in the aggregates seemed to give greater stability to aggregates of $<150\mu$. The presence of CO_2 gas in kaolinite after 20-minute shaking gave better aggregation than in the aggregates wetted under partial vacuum. Shaking in water in a shaker-bottle appeared to result in wearing down the surface rather than breaking up the aggregates into smaller particles.

The effect of the gaseous phase on water-stable aggregates is used to interpret some of the results found in the literature.

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PROPERTIES OF SOIL WHICH INFLUENCE WIND EROSION: I. THE GOVERNING PRINCIPLE OF SURFACE ROUGHNESS[1]

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Erosion of the soil by wind is influenced by numerous factors. Many useful methods of wind-erosion control have been devised through recognition of the importance of these factors in field experiments. Though such experiments have markedly increased our knowledge on how to hold the soil, they have not contributed appreciably to our knowledge of what constitutes an erodible or a nonerodible soil or of why some soils are more susceptible to erosion than others. Differences in erodibility suggest that inherent soil properties and properties brought about by cultivation and accelerated erosion play an important role.

To obtain more specific answers to these problems a series of experiments was undertaken. The first of the studies was conducted to gain more adequate information on the generally recognized but little understood relationship between erodibility of soils and their physical structure. A part of the results of these studies is herein reported. Another group of experiments was undertaken to evaluate the effects of various physical and chemical factors on the erodibility by wind.

SCOPE OF THE PROBLEM

Wind erosion is dependent directly on the physical condition of the soil. Only soils in a dry state are moved by wind; neither wet nor damp soils are affected appreciably. The structure of a soil in an air-dry state is, therefore, a more reliable index of erodibility than its structure in a wet state. The water-stable structure relates to erodibility; yet it is but one of many factors that determine the dry clod structure and erodibility (4).

Changes in dry clod structure which consequently affect the resistance of the soil to wind action are brought about by various field practices and environmental conditions. The more important of these are climatic and weather conditions (8), type of tillage and seeding implements employed (5, 12), soil moisture conditions at the time of tillage (14), and kinds of crops grown (10). Several attempts have been made to determine the erodibility of soils from the dry aggregate soil structure produced by various tillage and cropping treatments in the field (3, 13). A few attempts have been made to measure the relative erodibility directly by subjecting the soil to an artificial wind (9, 11).[3]

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[1] Contribution No. 410 from the department of agronomy, Kansas Agricultural Experiment Station, Manhattan, Kansas, and the Soil Conservation Service, U. S. Department of Agriculture. Cooperative investigations on the mechanics of wind erosion.

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The relationship between soil structure and erodibility by wind is intricate. Nevertheless, some attempts have been made to derive a formula simple enough for convenient use as a measuring stick of the erodibility of soils under various treatments in the field (3, 13). These measurements have been very useful but hardly adequate. A practical solution of the problem is needed for application in the field. Until this relationship is thoroughly understood and adequately expressed, it will be impossible to evaluate the importance of the different physical and chemical factors that affect the erodibility of the soil by wind.

The evaluation of the various factors that affect erodibility by wind falls logically into the second phase of the study. The literature reveals little study devoted to this relationship. Hardt (6) concluded from his investigations on soils in Bavaria that calcium carbonate is the chief factor responsible for erosion by wind, but that neither the size of grains nor the nature and amount of humus have any appreciable effect on erodibility. Hopkins (7) observed that soils high in calcium carbonate and in organic matter drifted badly in past years in Canada. He concluded that the fineness of soil structure is connected with the problem. Bradfield (1) affirmed that lime and organic matter do not in themselves ensure a good structure, such as is usually found in virgin soils, and concluded that much is yet to be learned concerning soil structure and the factors that affect it.

A series of investigations had been undertaken previously to find the relationship between soil structure and erodibility by wind (2, 3, 4). A graphical solution, based on experiments in a wind tunnel, was derived from these studies. This solution expressed the relationship between clod structure and erodibility. Because of the large number of constants that were found necessary to this approach, the formulas were too complicated for extensive use as a measure of erodibility of different soils. Consequently, an attempt was made to condense these into one simplified form applicable to the average effect of the most common erosive wind velocities. Experimental tests proved that the simplified form was valid within specific limits on a variety of soils of Western Canada (3).

Some important considerations pertaining to this problem have not been included in previous studies. One of these is a basic interpretation of the relationship between clod structure and erodibility by wind. The results of this study are presented herewith.

PROCEDURE

The soil materials used in this study were dune sand composed mainly of quartz grains, an alluvial fine sandy loam, a loessal silt loam, and an alluvial clay. They were thoroughly dried, passed through a nest of sieves, and stored in air-tight containers for use as required. To derive a simpler expression of erodibility than was possible in previous experiments (2), the limits of size of some fractions were broadened. The number of fractions was thus reduced from six to four. These were as follows:

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Fraction A—Highly erodible, <0.42 mm. in diameter.
Fraction B—Difficulty erodible, 0.42 to 0.84 mm. in diameter.
Fraction C—Nonerodible, 0.84 to 6.4 mm. in diameter.
Fraction D—Nonerodible, >6.4 mm. in diameter.

To test the erodibility of the soil materials, use was made of a closed-circuit type wind tunnel described previously (15). The tests were made under wind velocities of 18 and 25 miles per hour at a 6-inch height. These velocities are based on air with a density of 0.075 pound per cubic foot. An 18-mile-per-hour wind at a 6-inch height corresponds to a moderately erosive wind occurring commonly on the High Plains. A 25-mile-per-hour wind is infrequent, but the damage that occurs to soils on such occasions far exceeds that for lower velocities. The velocity of the wind was measured with a Pitot tube directly above the leeward end of the soil sample being tested and at various heights up to 6 inches. Velocities up to this height conformed to a definite pattern described previously for a position 48 feet downwind of the tunnel (15). The soil samples were exposed in a trough 5 feet long, 8 inches wide, and 2 inches high. The trough had open ends. It was placed in the downwind part of and parallel to the length of the test chamber. The remaining floor area of the test chamber, which was 54 feet long, 3 feet wide, and 3 feet high, was covered with nonerodible gravel 2.0 to 6.4 mm. in diameter. The gravel was smoothened or roughened as necessary to produce a surface roughness similar to that of the soil. The surface of the soil was leveled by hand in a layer 1.5 to 2.0 inches thick. Surface roughness and the thickness of the layer varied somewhat, depending on the size of the aggregates used. The trough was mounted on supports which could be raised or lowered to maintain the soil surface on the same level as that of the surrounding gravel.

The amount of soil erodible under a definite wind velocity was determined by weighing the material before exposure to the wind and after soil movement had ceased. A slight amount of dust circulated through the tunnel, but it was too fine to settle on the soil or to cause abrasion. During the course of the experiments temperature ranged from 70° to 85° F. and barometric pressure from 720 to 760 mm. of Hg. These variations do not appreciably affect the erosional force of the wind.

Measurements were also made of the average roughness of the surface before and after exposure to the wind. The roughness was measured by determining the height and the number of projections per unit area of ground.

RESULTS

In all soils containing erodible and nonerodible fractions the amount of soil removed under an erosive wind force was limited by the height and the number of nonerodible fractions that were exposed on the surface by the wind. On these soils, unaffected by encroachment of erodible material from the outside, the removal of the soil material continued until the height of the nonerodible projections and their number per unit area were increased to a degree that completely

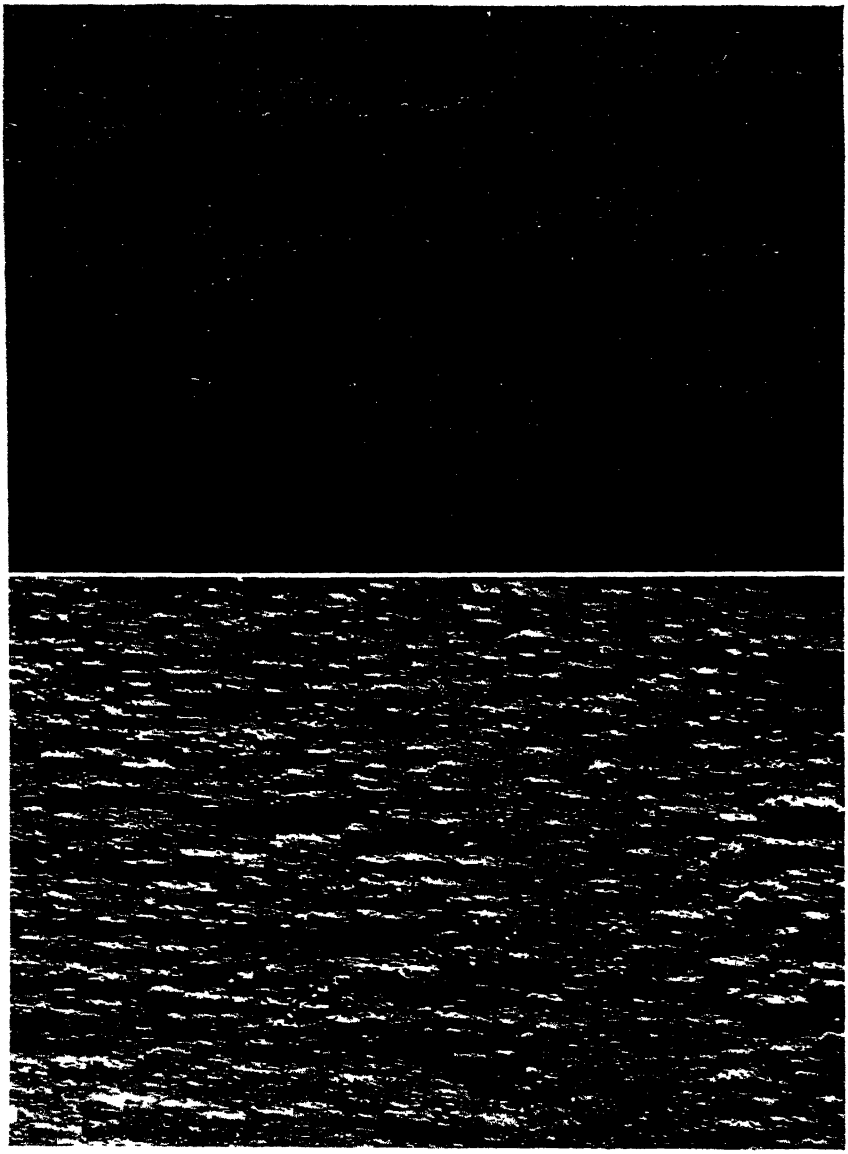

Fig. 1. Appearance of Silt Loam Soil Composed of 92 Per Cent of Fraction A and 8 Per Cent of Fraction C, (top) Before Exposure to Wind, (bottom) After Exposure Until Soil Removal Ceased

Wind velocity 18 miles per hour at a 6-inch height; wind direction left to right.

sheltered the erodible fractions from the wind. Movement then ceased (fig. 1). The time required for movement to cease ranged from about 0.5 to slightly more than 1 hour, depending on the structural condition of the soil (fig. 2). Two aspects of structure influenced the rate of removal: first, the smaller the size of the nonerodible clods present in the soil, the higher was the initial rate of removal and the shorter the time required for movement to cease; second, the larger the ratio of erodible to nonerodible fractions contained in the soil, the higher was the initial rate of soil removal and the longer was the time required for movement to cease.

If the soil contained a large proportion of erodible fractions, few nonerodible clods per unit area of ground became exposed by the wind. The nonerodible clods under such condition reached a very considerable height when soil removal ceased. If, on the other hand, the soil contained a small proportion of erodible fractions, large numbers of nonerodible clods were readily exposed by the wind. Removal of erodible fractions was thus restricted, and the height of the nonerodible projections reached when soil movement ceased was relatively low.

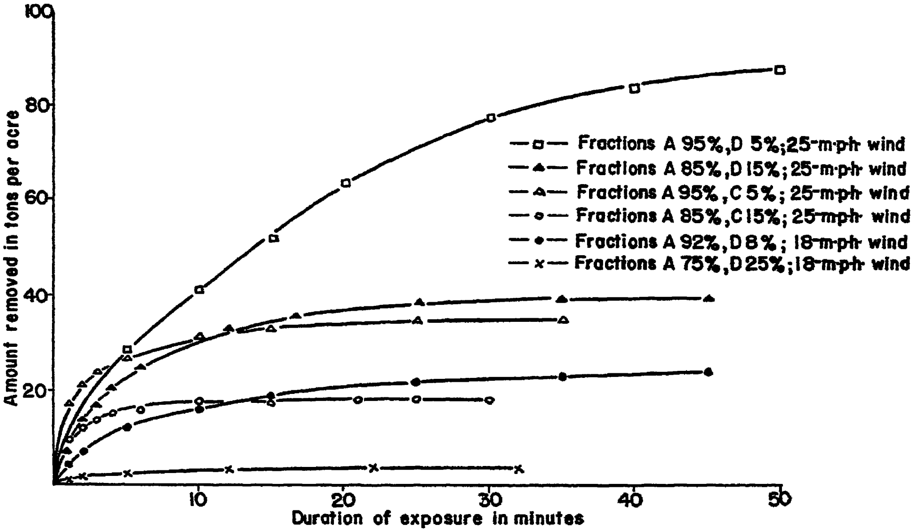

FIG. 2. RATE OF SOIL REMOVAL WITH DURATION OF EXPOSURE IN A WIND TUNNEL Length of soil area, 5 feet.

One important principle was clearly manifested in these experiments. At a stage when soil removal ceased, the height of the nonerodible projections divided by the distance between projections[4] remained constant for any proportion of erodible to nonerodible fractions present in the soil (fig. 3). This constant may be designated the *critical surface-roughness constant.* The constant may be defined as the ratio of height of nonerodible surface projections to distance between the projections which will barely prevent the movement of erodible soil fractions by the wind. The constant varied with wind velocity and with the size and specific gravity of the erodible fractions, but remained the same for the whole range of size and proportion (by volume) of nonerodible clods.

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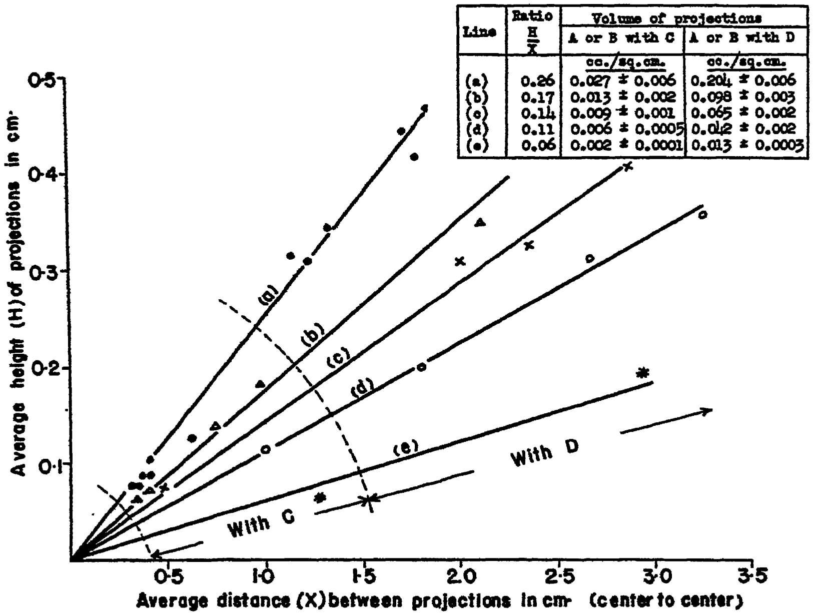
[4] Distance between projections is equal to $\sqrt{\frac{1}{N}}$ where N is the number of projections per unit area.

The critical surface-roughness constant reveals the basis for the peculiar relationship that exists between erodibility by wind and the structural condition of a cultivated soil. To examine this relationship more closely, let us take as examples two samples of soil: one, a highly erodible soil containing a ratio of 9 parts erodible to 1 part nonerodible fraction; the other, a wind-resistant soil having a ratio of 1 erodible to 1 nonerodible fraction. The relative distribution of the two fractions in each soil is represented diagrammatically and to approximate scale in figure 4. In the cross-sectional diagram the nonerodible fractions are represented by rough circles, indicating approximate spheres. The level of the bed before the wind was applied is indicated by a continuous line. The erodible fractions occupy the blank spaces between the circles and below the line. The volume V of a nonerodible fraction, assumed to be a sphere, is equal to $\frac{1}{6} \pi d^3$, where d is the diameter of the fraction. The average distance from the center of one nonerodible fraction in the soil to the center of the next along a horizontal or vertical plane is represented by X. Distance X is equal to $\sqrt[3]{V(R+1)}$ where R is the ratio of erodible to nonerodible fractions contained in the soil.



Line	Ratio $\frac{H}{X}$	Volume of projections	
		A or B with C	A or B with D
		cc./sq.cm.	cc./sq.cm.
(a)	0.26	0.027 ± 0.006	0.204 ± 0.006
(b)	0.17	0.013 ± 0.002	0.098 ± 0.003
(c)	0.14	0.009 ± 0.001	0.065 ± 0.002
(d)	0.11	0.006 ± 0.0005	0.042 ± 0.002
(e)	0.06	0.002 ± 0.0001	0.013 ± 0.0003

FIG. 3. RELATION OF HEIGHT OF SURFACE PROJECTIONS TO DISTANCE BETWEEN PROJECTIONS AFTER SOIL REMOVAL BY WIND HAD CEASED

(a) Sandy loam, silt loam, and clay, fraction A with C and A with D; (b) silt loam, B with C and B with D; (c) silt loam, A with C and A with D; (d) sandy loam, B with C and B with D; (e) quartz sand, B with C and B with D. Wind velocity for (a), (b), (d), and (e) was 25 m.p.h. and for (c) 18 m.p.h. at 6-inch height.

Under a highly erosive wind velocity (25 miles per hour at 6-inch height) removal of erodible fractions continued until the surface was lowered to the dotted line in figure 4. By drawing a straight line from the peak of one projection to the new surface at the base of the next projection to leeward, the angle to the horizontal varied from 4° to 12° depending on the size and apparent specific gravity of the erodible soil fractions.

Where the diameter of the nonerodible fractions was smaller than the height of the projections required to shelter the erodible bed, the descending grains struck the erodible bed and caused a rapid removal of the erodible particles. Under such conditions the nonerodible fractions (mainly fraction C) were undermined by removal of erodible particles from below them and slid to a lower level. This process continued until a sufficient number of nonerodible fractions were exposed by the wind to stop removal of the soil. The depth of the erodible layer was thus limited by the critical height and frequency of the nonerodible fractions that were exposed at the surface by the wind.

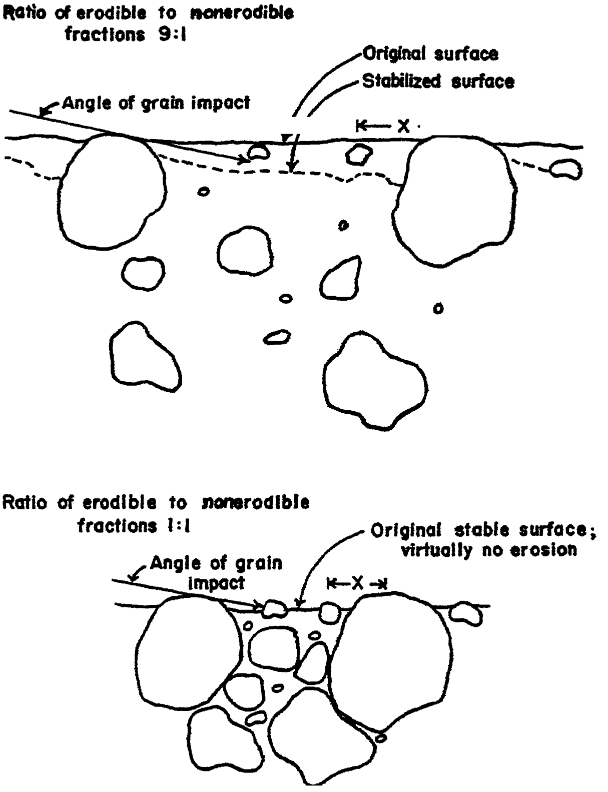

Ratio of erodible to nonerodible fractions 9:1
Original surface
Stabilized surface
Angle of grain impact
X
Ratio of erodible to nonerodible fractions 1:1
Original stable surface; virtually no erosion
Angle of grain impact
X

Fig. 4. Diagrammatic Representation of Amounts of Erosion with Two Different Proportions of Erodible to Nonerodible Fractions

Cross-sectional view through the maximum diameter of the nonerodible fractions.

Observations of the surface conditions produced by wind on various soils

TABLE 1

*Relation of amount of erosion to height, number, and volume of projections existing at the surface before and after exposure of soils to wind**

	25-MILE-PER-HOUR WIND AT 6-INCH HEIGHT																					18-MILE-PER-HOUR WIND AT 6-INCH HEIGHT			
	Fractions A and C						Fractions A and D				Fractions B and C				Fractions B and D	Fractions B and C	Fractions B and D			Quartz sand for B, clay for C	Quartz sand for B, clay for D	Fractions A and C	Fractions A and D		
a. Soil texture..............	Silt loam	Sandy loam	Silt loam	Silt loam	Silt loam	Sandy loam	Sandy loam	Clay	Silt loam	Clay	Silt loam	Silt loam	Silt loam	Silt loam	Silt loam	Silt loam	Sandy loam	Sandy loam	Sandy loam			Silt loam	Silt loam	Silt loam	Silt loam
b. Ratio of erodible to nonerodible fractions.........	95:5	90:10	85:15	75:25	60:40	50:50	92:8	85:15	75:25	60:40	90:10	75:25	65:35	60:40	90:10	92:8	90:10	75:25	60:40	95:5	95:5	92:8	92:8	85:15	75:25
c. Average height of projections before exposure *cm.*	0.010	0.040	0.044	0.063	0.076	0.079	0.159	0.144	0.201	0.332	0.016	0.064	0.067	0.067	0.198	0.01	0.139	0.168	0.220	0.01	0.164	0.01	0.168	0.218	0.310
e. Number of projections before exposure..*number/sq.cm.*	0.768	1.08	1.55	1.86	3.88	6.05	0.058	0.071	0.094	0.349	0.775	1.24	4.34	5.42	0.050	0.74	0.052	0.162	0.271	0.776	0.097	0.776	0.060	0.058	0.138
f. Average height of projections after exposure, *cm.*	0.106	0.125	0.088	0.087	0.079	0.079	0.469	0.419	0.445	0.310	0.181	0.139	0.070	0.071	0.352	0.118	0.361	0.312	0.203	0.059	0.194	0.073	0.410	0.326	0.313
g. Number of projections after exposure....*number/sq.cm.*	5.48	2.48	6.66	6.20	9.14	8.67	0.310	0.322	0.341	0.033	1.08	1.86	6.82	6.98	0.207	1.02	0.097	0.142	0.310	0.620	0.116	4.05	0.122	0.181	0.255
h. Volume of projections before exposure $(1/3\ \pi c^2(3r - c)e$ *cc./sq.cm.*	tr.	0.0009	0.0016	0.0037	0.0109	0.0182	0.0049	0.0049	0.0124	0.1208	0.0001	0.0025	0.0097	0.0121	0.0064	tr.	0.0034	0.0151	0.0427	tr.	0.0086	tr.	0.0056	0.0090	0.0419
i. Volume of projections after exposure $[1/3\ \pi f^2 (3r - f)g]$ *cc./sq.cm.*	0.0277	0.0168	0.0244	0.0223	0.0275	0.0261	0.2048	0.1723	0.2040	0.1924	0.0183	0.0151	0.0164	0.0173	0.0600	0.0063	0.0393	0.0437	0.0418	0.0011	0.0143	0.0121	0.0627	0.0605	0.0789
j. Volume of nonerodible fractions exposed by erosion.. $(i - h)$*cc./sq.cm.*	0.0277	0.0159	0.0228	0.0186	0.0166	0.0079	0.1994	0.1674	0.1916	0.0716	0.0132	0.0126	0.0067	0.0052	0.0736	0.0063	0.0359	0.0286	−0.0009	0.0011	0.0057	0.0121	0.0571	0.0515	0.0370

k. Weight of nonerodible fractions exposed by erosion (1.6*j*)† *gm./sq.cm.*	0.0443	0.0254	0.0365	0.0298	0.0266	0.0126	0.3190	0.2678	0.3006	0.1146	0.0212	0.0167	0.0107	0.0083	0.1178	0.0101	0.0574	0.0458	−0.0014	0.0018	0.0091	0.0194	0.0914	0.0824	0.0592
m. Weight of erodible fractions removed by erosion(*b k K*)..*gm./sq.cm.*	0.842	0.229	0.207	0.089	0.040	0.013	2.20	0.914	0.552	0.103	0.191	0.050	0.020	0.012	0.636	0.116	0.310	0.082	−0.001	0.034	0.104	0.223	0.631	0.280	0.107
n. Weight of erodible fractions removed by erosion (44.61 *m*)..*tons/A*	37.6	10.2	9.2	4.0	1.8	0.6	98.2	40.7	24.6	4.6	8.5	2.2	0.9	0.5	28.4	5.2	13.8	3.7	−0.05	1.5	4.6	9.9	28.1	12.5	4.8
o. Weight actually eroded in test tunnel..*tons/A*	35.7	15.6	11.1	5.4	1.6	0.6	80.5	40.2	22.4	7.1	7.1	1.9	1.0	0.6	20.8	4.1	10.4	3.0	0.5	1.3	2.8	8.1	22.0	12.1	4.9

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[*] Determination of the volume of projections is based on the assumption that the nonerodible fractions which form the projections are spherical, average radius (r) being 0.18 cm. for fraction C and 1.11 cm. for fraction D. Fraction C was, in fact, nearly spherical, but fraction D was very angular; hence, a shape coefficient K, 1.0 for fraction C and 0.6 for fraction D, is applied.

[†] Specific gravity of C and D = 1.6.

served as a basis for interpreting the relationship between the dry aggregate structure and erodibility. The data obtained (fig. 3) indicated that the ratio of the height of projections to the distance between them on a surface stabilized by wind was constant for any proportion and any size of the nonerodible fractions contained in the soil. The volume of the projections per unit area of ground, however, was not constant under any condition. In the great majority of cases the volume varied but little where the size of the nonerodible fractions remained the same. The extreme variation in volume occurred for mixtures of fractions A and C on loam soil. For these mixtures the maximum deviation from the average volume was 22 per cent. In most cases, however, this deviation did not exceed 5 per cent (fig. 3).

The height and number of nonerodible projections that existed on the soil surface before exposure to the wind had an important bearing on erodibility. Under uniform soil treatment, the height and number of surface projections increased with the concentration of nonerodible fractions contained in the soil. They varied also with the size of the nonerodible fractions (table 1). With relatively low concentrations of nonerodible fractions the surface was virtually devoid of any projections. Erosion by wind continued rapidly until a comparatively great depth of soil had been removed. With high concentrations of nonerodible fractions, on the other hand, the fine particles tended to sift downward among the coarser fractions, thereby forming a relatively rough surface composed predominantly of nonerodible clods. Consequently, the amount of erosion under such conditions was very small or none at all. When interpreting the effect of the height and number of surface projections on the erodibility by wind, it was necessary, therefore, to take cognizance of the volume of projections that occurred on the surface before, as well as after, exposure to the wind.

Observations on the actual surface roughness before and after exposure to the wind were recorded under different wind velocities, and these served as a basis of a mathematical interpretation of the relationship of soil structure to erodibility by wind. The volume of surface projections before exposure subtracted from the volume after the surface was stabilized by wind indicated the volume of the nonerodible fractions that was exposed by the wind. This volume multiplied by the ratio of erodible to nonerodible fractions contained in the soil indicated the volume of erodible fractions removable by wind (table 1). A comparison of these computed amounts with the actual amounts eroded in the wind tunnel showed a high degree of agreement between the two. The dominant principle which governs the erodibility of cultivated soils is evidently based on the height and number of nonerodible projections existing on the surface before exposure to the wind and on the critical surface-roughness constant of a stabilized soil. This principle can be expressed by an equation:

$$q = KRO_u (V_2 - V_1)$$

where q is the amount of soil erodible by wind; V_1 is the volume of the nonerodible projections existing at the surface before exposure, assuming projections are dome shaped; V_2 is the volume of such projections after soil movement has ceased; O_u is the density of the projecting units; R is the ratio of erodible to nonerodible fractions contained in the soil; and K is a coefficient the value of which depends on the actual shape of the projecting units.

V_1 varied directly with the proportion and size of the nonerodible fractions contained in the soil. V_2 varied considerably with wind velocity and with size and apparent specific gravity of erodible and nonerodible fractions (table 1). On the other hand, it varied little with the ratio of erodible to nonerodible fractions (fig. 3).

Apparent specific gravity of the highly erodible fraction A had little if any, influence on the height, number, and volume of surface projections exposed by wind [fig. 3, curve (a)]. Consequently, it had no appreciable effect on erodibility (tables 1 and 2). Apparent specific gravity of the semierodible fraction B, on the other hand, had a great influence on the number and magnitude of surface projections and on erodibility.

TABLE 2

Apparent specific gravity of various soil fractions used in wind tunnel experiments

SOIL FRACTION	DIAMETER	APPARENT SPECIFIC GRAVITY*			
		Quartz sand and gravel	Sandy loam	Silt loam	Clay
	mm.				
A	<0.42	2.65	2.10	1.84	1.66
B	0.42–0.84	2.65	1.72	1.48	1.56
C	0.84–6.4	2.65	1.50	1.45	1.53
D	>6.4	—	1.57	1.66	1.58

$$* \text{ Apparent specific gravity} = 2.65\left(\frac{\text{Weight of volume of soil grains}}{\text{Weight of same volume and size of quartz sand grains}}\right).$$

Apparent specific gravity of clods >6.4 mm. was determined by liquid displamecent method after the surface was coated with hot paraffin wax.

The shape of the nonerodible surface projections apparently influenced appreciably the amount of soil moved by wind. In all soils used, fractions C were spherical or nearly so. An assumption that surface projections composed of fractions C were sectors of a sphere of a given diameter was apparently valid (table 1). This assumption did not hold for fractions D, which were definitely more angular. If the surface projections composed of D were assumed to be sectors of a sphere of a given diameter, the computed erosion values were about twice the actual values. If, on the other hand, the projections were considered pyramidal, the computed erosion values were less than half, and if they were considered cubical more than six times the actual values. The actual shape of D projections, as indicated by coefficient K, was equivalent to that approximately half way between a spherical dome and a pyramid.

DISCUSSION AND CONCLUSIONS

For soils containing erodible and nonerodible fractions there is no definite wind velocity that will perpetuate the movement of soil material. Erosion continues until the nonerodible clods project sufficiently above the surface to give protection to the erodible fractions. Movement then ceases. In small fields, such as narrow strips, under wind of constant velocity blowing from one direction at right angles to the strip, the time required for movement to cease is relatively short (approximately 30 hours for a 20-rod strip). In large fields the time required is so much longer that soil removal under an erosive wind blowing from one direction does not cease. Nevertheless, the basis which determines the relative degree of erosion from small or large fields or from samples placed under an artificial wind in a tunnel appears to be the same. This basis is the amount of soil per unit area of surface erodible under some definite wind velocity. The rate of soil removal is not at all proportional to the total weight of erodible soil.

The frictional drag of the wind on the erodible particles immediately after soil removal has ceased is barely below that required to move the particles. The soil surface at this stage is stable and will remain stable as long as there is no increase in wind velocity, no change in wind direction, no breakdown of the nonerodible fractions by the forces of weather, and no abrasion. If for any reason the height of the projections is lowered or the distance between the projections is increased, as by forces of weather, removal of the erodible fractions on the previously stable soil will be resumed and will continue until the projections have again reached a height and lateral frequency required to stabilize the soil. At the ultimate stage of erosion much of the drag of an erosive wind is absorbed by the nonerodible clods protruding above the surface of the ground. Only the residual drag, which is just barely below that required to cause the erosion, is absorbed by the erodible fractions.

The amount of soil erodible by wind of some definite velocity is thus limited by the critical height of and distance between the nonerodible fractions that are exposed at the surface by the wind. The ratio of height of projections to distance between projections is designated as the critical surface-roughness constant. Under a given wind velocity the critical surface-roughness constant remains the same for the whole range of size and proportion of the nonerodible clods. The critical surface-roughness constant required to stabilize the soil varies with other factors, however, such as wind velocity and size and apparent specific gravity of the erodible fractions. These factors, in the aggregate, add considerably to the complexity of the phenomenon.

The critical surface-roughness constant determines, in part, the volume of the nonerodible projections exposed by wind erosion and, hence, the volume of soil removable by wind. The volume of the projections required to stabilize the surface under any given wind velocity and size and apparent specific gravity of the erodible fractions remains virtually constant throughout the whole range of proportion of erodible fractions contained in the soil. Consequently the amount of erosion can be said to vary almost proportionately, other factors being equal, with the ratio of erodible to nonerodible fractions contained therein.

The critical surface-roughness constant sets a limit to the amount of soil that may be removed by wind. The degree of surface roughness existing on the surface before exposure to the wind determines, on the other hand, how much soil may be removed before the critical roughness is reached. The volume of the surface projections before exposure is a function of soil structure. The more nonerodible fractions contained in the soil, the greater will be the volume of the nonerodible projections at the surface of the ground and the less the amount of erosion that will occur.

The volume of the surface projections before exposure to the wind subtracted from the volume after the surface is stabilized by wind indicates the volume of the nonerodible fractions exposed by erosion. This volume multiplied by the ratio of erodible to nonerodible fractions contained in the soil gives the actual volume of erodible fractions removable by the wind. The erosion values thus determined are approximately the same as the amounts eroded in the wind tunnel. The determinations thus present an insight into the general principle—the principle of surface roughness—that governs the erodibility of cultivated soils. The principle of surface roughness gives the basis for the peculiar relationship which exists between soil structure and erodibility by wind. It involves the effect of three sets of factors all of which relate to the degree of surface roughness. These factors are: (*a*) the volume of surface projections determined at the outset by the size and proportion of nonerodible clods; (*b*) the ratio of erodible to nonerodible fractions contained in the soil; (*c*) the size, shape, and apparent specific gravity of erodible and nonerodible fractions. This paper gives merely an indication of the effect of these factors on surface roughness and erodibility.

SUMMARY

The amount of soil erodible by wind is limited by the critical height of and distance between the nonerodible fractions that are exposed at the surface by the wind. Erosion ceases as soon as this critical stage is reached. The ratio of height of surface projections to the distance between projections after soil removal has ceased remains constant irrespective of the size and proportion of the nonerodible clods contained in the soil. The ratio varies with other factors, however, such as wind velocity and size, shape, and apparent specific gravity of the erodible fractions. These factors, as a whole, add considerably to the complexity of the erosional phenomenon.

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BOOKS

Annual Review of Microbiology. Edited by CHARLES E. CLIFTON, SIDNEY RAFFEL, AND H. ALBERT BARKER. Annual Reviews, Inc., Stanford, California, 1949. Pp. 476. Price $6.

This is volume 3 of this series. It contains careful reviews of the literature on 18 selected topics in microbiology, including bacterial variation, actinomycetes, ciliated protozoa, metabolism and nutrition of microorganisms, constituents of viruses, antibiotics *in vivo*, immunity, virulence and pathogenicity, acquired immunity, chemistry of toxins, disease resistance in plants, oral microbiology, dermatropic viruses, food microbiology, growth of bacterial cultures, techniques, and bacteriophage. The authors include Lederberg, Erikson, Sonneborn, Umbreit, Snell, Knight, Cutting, Taliaferro, Watson, Brandly, Raffel, Pillemer, Robbins, Hart, Harrison, Buddingh, Halvorson, Monod, McClung, and Fong. Reference is made to the work of some 2,500 authors. These reviews are of great value to microbiologists, but they are of even more importance to workers in other fields of biology who are less familiar with recent developments in microbiology but need to be kept informed concerning them. All scientists are greatly indebted to the men who prepare, edit, and publish these reviews.

Antibiotics. Edited by GEORGE W. IRVING AND HORACE T. HERRICK. Chemical Publishing Co., Inc., Brooklyn, 1949. Pp. 273. Price $6.75.

The chapter on antibiotics from higher plants is of special interest to soil-plant scientists in that it suggests "possibilities for the successful large-scale use of such antibiotics in the control of plant disease." It contains references to 138 papers that have been published in this field of research. The other 13 chapters in the book deal with the history and development of the more common antibiotics, especially penicillin and streptomycin. Some of the other antibiotics that have been found toxic to animals are believed to have possible value in the control of plant pathogens. The several chapters are lectures that were delivered by some of the most prominent men engaged in this field of research, including Cragwall, Dubos, Folkers, Heishman, Herrick, Irving, Keefer, Raper, Robbins, Waksman, Welch, and Wintersteiner. Those who are concerned with organic-matter relationships in soils may find it worth while to explore the book for possible suggestions in the use of green manures as agents for the control of soil-borne plant-disease organisms.

Colorimetric Methods of Analyses. Third Edition. FOSTER DEE SNELL AND CORNELIA T. SNELL. D. Van Nostrand Company, Inc., New York, 1949. Pp. 950, figs. 51. Price $12.

About one quarter of the papers on analytical chemistry that are now being published are in the field of colorimetry. That explains the reason for and the importance of this volume. Methods are presented for the determination of some 60 elements and, in addition, of the several forms of some of these elements. Several methods are usually given for each element, the choice depending upon the quantity of the element present, the availability of reagents, and the apparatus at hand. Reference is made to the work of more than 2,000 analysts. The material is concisely presented but in sufficient detail to meet most requirements. The authors have made a highly important contribution to the literature in this field. Every analytical laboratory will want a copy of the book close at hand for ready reference.

Grass Silage and Dairying. By RAY W. INGHAM. Rutgers University Press, New Brunswick, New Jersey, 1949. Pp. 88. Price $1.50.

The book presents the results of a 5-year research project that was financed by the Herman Frasch Foundation and carried out under the direction of Willis A. King, Walter C. Russell, and Carl B. Bender. Its purpose is to present the case for grass silage in comparison with corn silage. The key to the presentation is found in the statement: "Even making allowance for the 10 per cent loss of nutrients considered nominal and unavoidable in the preparation of grass silage, properly ensiled 'greens' can satisfactorily replace some of the concentrates, a large part of the hay, and all of the corn silage in the barn ration."

The addition of molasses is essential for dependable results, the amount varying between 40 pounds per ton for the grasses, 60 for mixed grasses and legumes, 80 for perennial legumes, and 100 for soybeans. The book is written in nontechnical language for the widest possible use of readers who are primarily concerned with dairy-farm practice. Seven tables of data from the original research report are given in the appendix.

Introduction à L'Étude Pédologique des Sols du Territoire du Bas Fleuve. By J· MEULENBERG, with the collaboration of L. de Leenheer and G. Waegemans· Librairie Falk fils, Georges van Campenhout, Successor, Brussels, 1949. Pp· 133, figs. 23, plates 6.

This is a paper-bound publication reporting on a preliminary study of the soils and vegetation of the Belgian Congo. Following some general considerations of the possible agricultural importance and development of the area, the authors outline the pedogenic factors, the forests, the agricultural value of the soils, the regeneration of the forests, and some conclusions with respect to the cartography of the land. An example of the survey maps, in color, is shown. A bibliography of 29 references is appended, as well as 50 excellent photographs of the soil, topography, and vegetation of the area.

Laboratory Manual for Students in Agronomy. Sixth Edition. by L. F. GRABER AND H. L. AHLGREN. Wm. C. Brown Company, Dubuque, Iowa, 1949. Pp. 204.

This is a paper-bound, loose-leaf laboratory manual designed for students in the first course in farm crops at agricultural colleges. The beginning exercises deal with land utilization in the United States, developments in population, farm income, livestock production, and crop distribution and acreages. The later ones give detailed consideration to corn, small grains, grasses, and legumes. The illustrations are excellent guides to the student, who is encouraged to think his way through the mass of facts to a well-organized set of morphological, physiological, ecological, and genetic principles that can be widely applied. A list of questions is appended to each chapter, and a more extended set of practical farm problems completes the course. A glossary of terms is appended. The course is designed to have cultural as well as practical value. Instructors in farm crops will find material of considerable value to them in this manual, and many of them may decide that it meets all their needs.

Relation of Soil Content to Human Longevity. By T. J. BROOKS AND T. J. BROOKS JR. Department of Agriculture, Tallahassee, Florida, 1949. Pp. 116.

This is a largely a collection of comments of a great variety of men who have had something to say on the subject. The most interesting feature of the book is a diagrammatic presentation of the alimentary tract of man as a food factory. It is evident from the material quoted that many men of greater or lesser standing as scientists have some definite ideas on this subject. The validity of many of the concepts, however, is extremely doubtful, and the authors do not contribute much toward a clarification as to what is fact and what is fancy. Nevertheless the pamphlet makes very interesting reading.

Soil, Food, and Health. Edited by JONATHAN FORMAN AND O. E. FINK. Friends of the Land, Columbus, Ohio, 1948. Pp. 342. Price $4.50.

The subhead "You are what you eat" indicates the general purpose of this book, which reports the proceedings of the seventh annual conference on conservation, nutrition, and health and some integrating essays from previous conferences. The topics considered include water, sewerage, forestry, soil fertility and health, vitamins and minerals in vegetables, genetics, nutritional needs of livestock, population pressures, world's foody supply, animal agriculture, diet and aging, plans for the future, and grass "as the master food." One gets the impression from reading this book that the authors of the papers are searching for truth through a maze of miscellaneous facts and fancies. The general approach to the problem is interesting and useful. A number of highly capable men are included in the list of authors.

THE EDITORS

Soils, Their Physics and Chemistry. By A. N. PURI. Reinhold Publishing Corp., New York, 1949. Pp. 550, figs. 59. Price $7.

This is an important book. It represents the point of view of a well-trained physical chemist who has spent the greater part of his life in relative isolation from other workers in soil science, except by way of the printed pages of technical journals. The book consists largely of a record of the author's researches in soils during the last 25 years. It is divided into three parts: chemistry of the soil, mechanical analysis of soils, and soil moisture. It contains 58 chapters. There are no references. Occasional mention is made of some other research worker, but this is only incidental to the development of certain simplified concepts that are employed to explain all the known phenomena of the subjects with which the book is concerned. The book merits a wide reading and it is quite likely to get it, once it falls into the hands of the younger soil scientists who need this type of readily understood presentation of the subject as a basis for further study.

MECHANISM OF ZINC FIXATION BY COLLOIDAL CLAYS AND RELATED MINERALS

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Zinc is an essential element for plant growth. Some soils contain appreciable amounts of zinc that plants are unable to utilize. Addition of zinc compounds to such soils is of little benefit, for zinc becomes fixed. In this paper the problem of zinc fixation is examined in the light of crystal chemistry.

TERMINOLOGY

Clays and many other aluminosilicates exhibit the phenomenon of ion interchange. If they are treated with a solution containing zinc salts, Zn is adsorbed and held in exchangeable form. It may be displaced by neutral salts such as KCl or neutral ammonium acetate.

Not all of the adsorbed zinc is replaceable. A portion is fixed in nonreplaceable form. In this paper the term *fixed zinc* denotes that amount of adsorbed zinc which cannot be released by leaching with neutral normal ammonium acetate.

Clay leached with neutral normal ammonium acetate takes up NH_4^+. After removal of occluded NH_4-acetate with methyl alcohol, the adsorbed NH_4^+ may be determined by distillation with MgO. The ammoniated clay is designated as *NH_4-clay*, and the amount of NH_4^+ adsorbed (milliequivalents of NH_4 in 100 gm. air-dry clay) constitutes its cation-exchange capacity or NH_4-capacity. This capacity is influenced by the previous treatment of the clay.

Clay leached with zinc salts becomes Zn-clay.

Subsequent treatment with NH_4-acetate converts the Zn-clay into NH_4-(Zn-clay) containing exchangeable NH_4 and fixed zinc.

TYPE OF CLAYS STUDIED AND EXPERIMENTAL METHODS

Wyoming bentonite; kaolinite from McNamee Mines, S. C.; Mg-clay from Hector, California[3]; muscovite; biotite; talc (from W. P. Kelley's collection); brucite; and vermiculite all ground to pass a 100-mesh sieve, were used in this investigation (fig. 1). Zinc-saturated minerals were prepared by treating each mineral as follows: The suspensions were heated over the steam bath for 24 hours and then leached with normal zinc acetate until completely saturated with zinc. Excess zinc acetate was removed with 50 per cent methyl alcohol. Exchangeable zinc was determined by leaching varying amounts of the zinc-saturated minerals with about 500 ml. of neutral normal ammonium acetate. The leachate was analyzed for zinc by means of the polarograph. In the fused material, total zinc was likewise determined.

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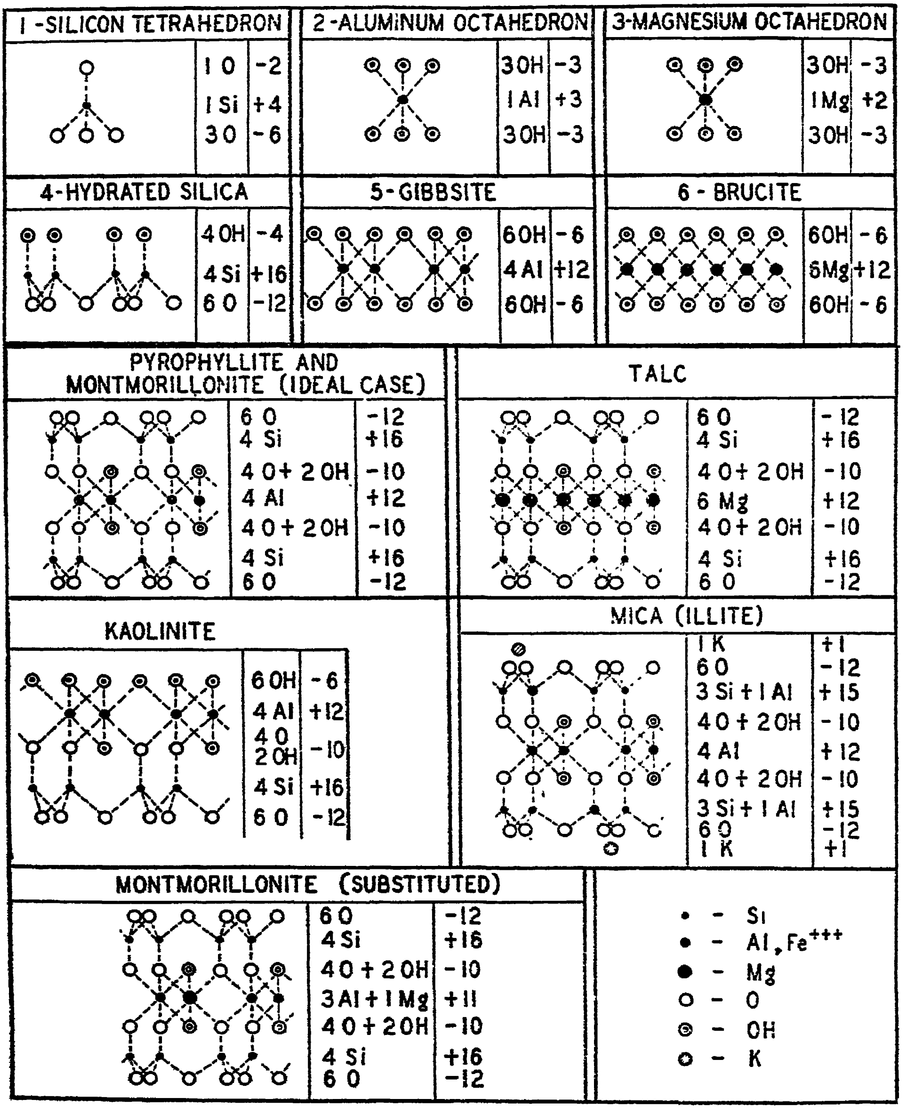
[1] Assistant professor of soil science, Farouk I University, Alexandria, Egypt. The author wishes to express his gratitude to Hans Jenny for his valuable help and suggestions during the work.

[2] Temporarily withdrawn, resubmitted October 4, 1949.

[3] Foshag, W. F., and Wooford, A. C. Bentonitic magnesium clay from California. *Amer. Mineral.* 21: 238–244. 1930.



Courtesy Ernst A. Hauser and the Journal of the American Ceramic Society

FIG. 1. STRUCTURAL REPRESENTATION OF SOME OF THE MINERALS STUDIED
Positive and negative charges are indicated in each case. After Hauser[4].

Chloride adsorption from HCl by both NH_4-clay and NH_4-(Zn-clay) was also studied. Furthermore, NH_4-saturated Mg-clay, vermiculite, talc, and brucite were analyzed for total magnesium. Zinc-saturated Mg-clay, vermiculite, talc, and brucite were analyzed for both total magnesium and total zinc.

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[4] Hauser, E. A. Colloid chemistry in ceramics. *Jour. Amer. Ceramic Soc.* 24: 179–187. 1941.

EFFECT OF ZINC TREATMENT ON NH_4-CAPACITY AND ADSORPTION PROPERTIES OF MINERALS

Pertinent information is gained by comparing the NH_4-exchange capacities of the original and the zinc-treated minerals (table 1). The nine minerals studied fall into three distinct groups; namely, those which sustained, as a result of zinc adsorption,

TABLE 1

Effect of zinc saturation on cation-exchange capacity and chloride adsorption of clays and other minerals

All values are expressed as milliequivalents per 100 gm. of oven-dry material

MINERAL	NH_4-CAPACITY			ZINC IN MINERAL			Cl ADSORPTION FROM 4S HCl BY NH_4-(Zn-Mineral)*
	Original mineral (NH_4-mineral)	Zn-treated mineral [NH_4-(Zn-mineral)]	Change	NH_4Ac Replaceable	Total	Fixed	
Bentonite	92.0	84.5	−7.5	120.2	129.2	9.0	0.0
Kaolinite, ground 13 days	15.2	10.5	−4.7	22.3	29.1	6.8	4.1
Kaolinite, ground 6 days	31.4	18.5	−12.9	31.6	62.1	30.5	26.2
Pyrophillite, ground 6 days	17.0	11.5	−5.5	21.1	31.0	9.9	1.5
Muscovite	33.6	16.2	−12.4	33.8	58.3	24.5	3.1
Biotite	7.8	5.1	−2.7	29.7	52.2	22.5	0.0
Mg-clay	31.6	31.4	−0.2	451.5	577.5	126.0	0.0
Vermiculite	36.5	37.2	+0.7	76.0	420.0	344.0	...
Brucite	0.5	0.45	−0.05	996.0	1320.0	324.0	0.0
Talc	12.4	34.4	+22.0	105.4	240.0	134.6	...

* NH_4-(Zn-mineral) denotes minerals having exchangeable NH_4 but nonexchangeable (fixed) Zn.

1. A diminution in NH_4-capacity: bentonite, kaolinite, pyrophyllite, muscovite, and biotite.
2. No significant change in NH_4-capacity: Mg-clay, vermiculite, and brucite.
3. Increase in NH_4-capacity: talc.

On theoretical grounds, any change in the NH_4-capacity of a given mineral powder is the result of variations in the amount and kind of the positive and negative ions that make up the particles. According to the principle of electrostatic neutrality,[5] this alteration must be such that the sum of the positive and negative valencies residing inside and on the surface of the crystal remains zero. It is of interest to examine, in light of this principle, the chemical changes that accompany zinc fixation.

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[5] Paulin, G. L. Nature of the Chemical Bond and the Structure of Molecules and Crystals. Cornell Univ. Press, Ithaca, N. Y. 1940.

A decrease in the NH_4-adsorption capacity of a mineral results from diminution of the total negative charge of its lattice. This would happen if positively charged ions enter the lattice, either to substitute for ions of lower valence or to become an integral part of the mineral without ion substitution. The cations that thus become incorporated within the lattice framework would be strongly held and no longer available for exchange and hence are considered as being fixed by the clay. On this basis, the difference between total adsorbed zinc and zinc replaceable by ammonium acetate may be considered as fixed zinc. If this fixed portion of zinc actually entered the lattice without substitution for other ions, the electrostatic neutrality principle would require that introduction of 1 millimol of divalent zinc be accompanied either by adsorption of 2 me. of anions or by a decrease of 2 me. of the cation-adsorption capacity.

Table 1 shows that a fixation of 9.0 me. zinc by bentonite was accompanied by a decrease in the NH_4-capacity of 7.5 me. per 100 gm. On the other hand, in kaolinite and muscovite, the amount of fixed zinc exceeded the decrease in NH_4-capacity. To satisfy the electrostatic neutrality of the mineral, both kaolinite and muscovite do exhibit anion adsorption properties when pretreated with Zn.

POSSIBLE POSITIONS OF FIXED ZINC IN CRYSTAL LATTICES

Since fixed zinc is no longer replaceable, it is possible that it has entered the lattice. Cavities of comparable sizes are furnished by the unoccupied holes in the Al octahedral layer of the lattice.

For an ion to enter the lattice, it is essential that there be openings through which the ion can move. Since ions are not rigid spheres and can assume different configurations within certain limits, the size of the openings need not necessarily be equal to that of the ion. In minerals with Si-Al structural pattern, ons may enter the lattice through the holes produced by the distorted Al-octahedra on the a-b planes. In minerals with Si-Al-Si structure, however, entrance of the ion through the Si-O-planes seems improbable. In such a case the easiest way for an ion to be incorporated within the lattice is to pass through holes on the broken surfaces.

The amount of zinc fixed by kaolinite was found to increase with grinding. Table 2 shows the amounts of exchangeable zinc, total zinc, and zinc fixed as a function of grinding.

The increase in the amount of zinc, both adsorbed and fixed, on grinding may be attributed to the newly exposed surfaces. If grinding mainly causes breaks across the lattice, more broken surfaces would be exposed; whereas if it mainly shears the packets apart, new 001 planes would be produced. In both cases zinc would find its way into the lattice through the newly exposed surfaces. It is to be noticed that kaolinite ground for 12 days has less capacity to fix zinc than that ground for 9 days. This may be due to destruction of the lattice structure.

ADSORPTION OF ZINC AS A COMPLEX ION

Zinc was found to be adsorbed partly as monovalent complex ion and then become a part of the inner layer of the electrical double layer. This type of zinc adsorption had been thoroughly discussed for bentonite clays[6]. Further investigation of this type of zinc adsorption by other minerals seems to confirm the results found for bentonite. Table 1 shows that for all minerals studied the amount of zinc released by ammonium acetate exceeded NH_4^+ ions adsorbed. This had been explained as due to the release of some of the monovalent zinc ion. It appears that minerals vary greatly in their selective adsorption of the monovalent zinc ions and hence in the relative amounts of zinc fixed within the inner layer. Data at hand[7] indicate that the capacity of kaolinite to adsorb monovalent zinc exceeds that of bentonite.

SUBSTITUTION OF ZINC FOR MG IN CRYSTAL LATTICES

Table 1 shows that the minerals Mg-clay, vermiculite, and brucite do not change their NH_4-capacity as a result of zinc treatment and that the NH_4-(Zn-minerals) do not possess the property of anion adsorption. They do, however contain large amounts of fixed zinc, greatly in excess of the original ammonium acetate capacities.

TABLE 2

Fixation of zinc by kaolinite as influenced by time of grinding

All values are expressed as milliequivalents per 100 gm. oven-dry kaolinite

NUMBER OF DAYS	TOTAL ZINC	NH_4-REPLACEABLE ZINC	FIXED ZINC
0	10.2	2.8	7.4
3	29.1	15.6	13.5
5	68.2	28.4	39.8
9	94.4	49.1	45.3
12	73.1	50.8	22.3

These facts suggest that fixed zinc must have taken the place of ions of equal valency. To have a stable structure, the ion replaced by zinc should be of similar ionic radius. The fact that these minerals contain Mg, which has an ionic radius almost identical with that of zinc (Mg = 0.78 A. and Zn = 0.83 A., according to Goldschmidt), suggests that zinc may have taken the place of magnesium. If such is the case, zinc adsorption must be accompanied by an equivalent decrease in the magnesium content of the minerals. This is approximately the case with Mg-clay and talc, as indicated by table 3, which shows the Mg and Zn contents of the NH_4- and the Zn-saturated minerals.

In brucite no equivalence exists between zinc taken up and magnesium removed. This discrepancy may be explained by partial dissolution of brucite in aqueous zinc acetate solutions.

The mechanism of substitution may be explained as follows: On grinding, cleavage is favored in places where the bond strength is weakest. In minerals with Si-Al-Si structures, cleavage takes place between the planes where weak Van der Waals forces operate. In minerals with Mg in octahedral positions the bond strength between each Mg and O or OH ion is relatively weak (⅓ unit) and the lattice may be torn horizontally through the octahedral plane. This results in exposure of numerous Mg ions on the broken surfaces. These Mg ions are the ones replaced by zinc in the process of zinc adsorption. The fact that ammonium acetate replaces larger amounts of zinc than does barium acetate is probably due to a dissolution effect. Similar explanation was given by Kelley and Jenny[8] for the leaching of Mg from talc by ammonium acetate without equivalence adsorption of NH_4^+.

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[6] Elgabaly, M. M., and Jenny, H. Cation and anion interchange with zinc montmorillonite clays. *Jour. Phys. Chem.* 47: 399–408. 1943.

[7] Elgabaly, M. M. Mechanism of zinc adsorption and fixation by certain clay and other minerals. Ph.D. Thesis, Univ. of Calif., Berkeley. 1943.

TABLE 3

Effect of zinc saturation on magnesium and zinc content of ground minerals

All values are expressed as milliequivalents per 100 gm. of oven-dry mineral

MINERAL	ZINC		Mg CONTENT			TOTAL ZINC*
	NH_4-acetate replaceable	Ba-acetate replaceable	NH_4-mineral	Zn-mineral	Decrease	
Mg-clay	451.5	75.5	1522.0	966.0	556.0	577.5
Vermiculite	76.0	76.0	1350.0	996.0	354.0	420.0
Talc	105.4	36.8	1515.0	1269.0	246.0	240.0
Brucite	996.3	5.0	3450.0	689.0	2761.0	1320.0

* Based on fusion analysis.

TABLE 4

Replacement of fixed zinc by $MgCl_2$

All values are expressed in milliequivalents per 100 gm. oven-dry material

MINERAL	ZINC CONTENT		Mg CONTENT	
	Before leaching with $MgCl_2$	After leaching with $MgCl_2$	Before leaching with $MgCl_2$	After leaching with $MgCl_2$
Mg-clay	577.0	300.0	966.0	1250.0
Talc	240.0	185.0	1269.0	1450.0
Brucite	1320.0	1285.0	689.0	740.0

RESUBSTITUTION OF FIXED ZINC BY MG

Since Zn substitutes for Mg in minerals having Mg in octahedral position, the following experiment was conducted to find out whether this fixed zinc can be replaced by Mg.

To 3-gm. samples of each of the Zn-saturated talc, Mg-clay, and brucite, 3 gm. of $MgCl_2$ was added. The mixtures were placed in a platinum dish, wetted, and heated in the muffle to 400°C. for 6 hours. Brucite was heated to 125°C. only. Subsequently, the minerals were leached with *N* $MgCl_2$ until no zinc could be detected in the leachate. Excess $MgCl_2$ was then removed with 95 per cent methyl alcohol. Zn and Mg were determined both in the leachate and in the leached minerals. The results are shown in table 4.

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[8] Kelley, W. P., and Jenny, H. The relation of crystal structure to base exchange and its bearing on base-exchange capacities in soils. *Soil. Sci.* 41: 367–382. 1936.

It is evident that zinc fixed by the clay mineral cannot be replaced wholly by Mg. In other words, the reaction is not entirely reversible for the treatment used in this experiment.

AGRICULTURAL SIGNIFICANCE OF THE PROBLEM

It is often mentioned in the literature that the availability of the minor elements for plants depends greatly upon the pH of the growth medium. Deficiency symptoms are attributed often to high pH values, which cause precipitation of ions in forms not readily available to plants. Though this may offer an explanation in many cases, the present study suggests additional possibilities. The fact that zinc can substitute for magnesium in minerals with Mg in octahedreal coordination makes it rather difficult for the plants to get their zinc requirements. Moreover, small additions of zinc to such soils may give little or no response. Likewise manganese and copper would be expected to behave in a way similar to zinc under comparable conditions. Such postulations, however, must await further experimentations.

SUMMARY AND CONCLUSIONS

Zinc adsorption was studied with various minerals of known crystal structure. A fraction of the adsorbed zinc was found to be nonexchangeable with ammonium acetate and is considered as being fixed by the mineral.

In minerals with Al in octahedral arrangement, zinc is thought to be fixed in the holes not occupied by Al ions. This type of fixation is accompanied by a decrease in the cation-adsorption capacity and an increase in the anion-adsorption of the mineral.

In minerals with Mg in octahedral positions zinc substitutes for Mg. This process does not affect the adsorption properties of the mineral.

Some of the zinc adsorbed on the surface (complex monovalent form) may enter the inner layer of the electrical double layer, where it cannot be exchanged with neutral inorganic salts.

Magnesium cannot completely replace all the zinc taken up by the minerals.

The aforementioned facts suggest that soils containing clays with low Si/Mg ratios may fix zinc in forms not readily available to plants.

INFLUENCE OF EARTHWORMS ON SOIL MICROORGANISMS[1]

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The role of earthworms in the soil has been studied for at least a hundred years, and volumes have been written about the physical and chemical transformations for which they are responsible or are thought to be responsible. There are also numerous references in the literature stating or assuming a belief in an influence of earthworms on soil microflora. Usually, these references have reported only observations on the microflora of soils in which earthworms were present or absent, without establishing any causal relationship.

It has been a matter of common observation that nitrification is more active in worm-inhabited than in other soils (3, 5, 6, 9, 10, 12, 13, 14, 15, 17, 20, 22). This phenomenon has been severally attributed to heightened soil aeration (3), to alkaline fluids in the digestive tracts of the worms (5), to the decomposition of the bodies of dead earthworms (21), and to a higher nitrogen level where a predominantly fungal population is controlled by faunal feeding (19).

There is less information concerning changes in soil microflora which may take place in the digestive tract of an earthworm. Bassalik (2) isolated more than 50 species of bacteria from the alimentary canal of *Lumbricus terrestris* L. and could find no qualitative difference in the bacterial flora of the soil from which the worms came, of the gizzard, of intestinal contents, and of feces. Unfortunately, Bassalik's work was hardly quantitative. Aichberger (1) filled in the details for the larger organisms. He observed that the crops, gizzards, and intestines of earthworms contained extraordinarily few larger organisms not possessing firm outer coats. No desmids, diatoms, blue-green algae, yeasts, rhizopods, or other organisms were found alive. Stöckli (23) showed that virtually all the species and physiological groups sought were present in greater numbers in earthworm castings than in soil. He likewise showed that bacterial numbers in castings increased for 5 days after the castings were voided. Though Stöckli's work shed much light on the changes which may be expected to take place in soil, he admitted that he did not distinguish between the direct effect of the worm's digestive tract and that of worm-induced physical changes in the soil on bacterial flora. It also appears likely from the description of his sampling method that the soil used for comparison was not identical with that from which the castings were formed. Apparently, further progress requires quantitative comparison of the flora in the soil which is ingested by the worm and that in the fresh excrement which is derived from this soil. The experiments reported in this paper were undertaken to provide some information of this kind.

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[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University—the State University of New Jersey, department of microbiology.

EXPERIMENTAL

Total numbers of microorganisms in soil and in castings

In order that experimental results might be assigned to definite species, each worm was tested separately, then killed and identified. In some cases, the clitellum was lacking throughout the entire period of observation, making positive identification impossible, but all specimens were believed to be *L. terrestris* L. (fig. 1).

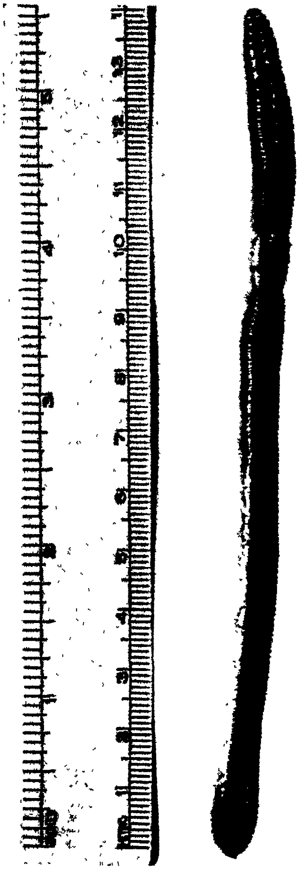

Fig 1

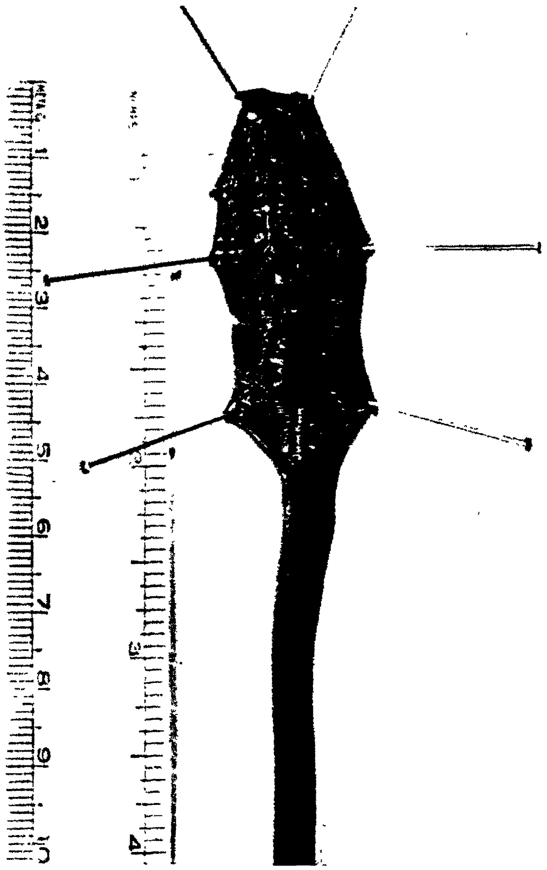

Fig. 2

Fig. 1. *Lumbricus terrestris* L.

Fig. 2. Anterior end of digestive tract of *L. terrestris*

Each worm was taken from a common storage pot, and all soil clinging to it was carefully washed off with tap water. To replace the soil in its intestine, it was placed, for at least 24 hours, in a pot of the soil to be tested. As the soils of the storage pots and of the test pots were of different colors, the color of castings being voided showed when the replacement was complete. Another pot of the test soil was then tamped firmly enough to prevent the earthworm from making a burrow merely by nosing its way between the particles. The worm was placed in the pot and, as it was forced to eat its way into the soil, castings were voided and left on the surface where they could be collected easily. These castings were collected as soon as possible, weighed, diluted by a series of water blanks, and used for the inoculation of plates or flasks of liquid media.

Ten grams of the soil in the test pot was weighed out, diluted in the same manner, and inoculated at the same time into plates or flasks of media. The soil of the pot from the surface of which the castings were collected was used for comparison. This was done to avoid the possibility that the flora of the transfer pot might have been more or less altered by the worm inhabiting it for 1 to 3 days and bringing to it an alimentary canal charged with a different kind of soil. Results are shown in tables 1, 2, and 3. The figures do not represent replications but repetitions with samples collected at different times.

Species and groups of bacteria in soil and in castings

The failure of earthworms to exert on total populations an influence that was constant in either direction or degree, pointed clearly to a study of their effects upon definite groups of bacteria as the logical next step. For their study three groups were selected: (*a*) the nitrifying bacteria—ammonia oxidizers and nitrite oxidizers separately—because of their importance in soil and because of the often-reported superiority of earthworm castings or of mull humus layers in nitrate content; (*b*) *Serratia marcescens* as a representative of the gram-negative non-spore-forming bacteria; (*c*) *Bacillus cereus* var. *mycoides* as a representative of the spore-forming bacteria. The procedure used for comparing the numbers of nitrifying bacteria in soil and in castings was as follows: Soil and fresh castings formed from that soil were diluted from 1 in 10 to 1 in 200,000, and 1 ml. of each dilution was used as inoculum for 50 ml. of a modified Winogradsky $(NH_4)_2SO_4$ or $NaNO_2$ medium (8) in liter Erlenmeyer flasks. After 3 weeks of incubation, each flask was tested weekly with Trommsdorf reagent (7) for the formation of nitrates and with brucine, after removal of the nitrites by boiling with sulfanilic acid, for the formation of nitrates. Contrary to the testimony of Lunge and Lwoff (16), a positive brucine test was obtained with the $NaNO_2$ medium used. The nitrate test was checked with sulfanilic acid and alpha-naphthylamine. Seven or eight weeks usually elapsed before it was apparent that nitrites or nitrates would not form in any higher dilution. By repetition it was possible to narrow the range of dilutions until the point of extinction was rather closely approximated. Only the final series are reported in table 4.

S. marcescens and *B. cereus mycoides* were studied by comparing castings with soils which had been heavily inoculated with these organisms. A soil was first moistened and mixed; then a cupful was poured into each of three pots. To one pot was added 5 to 15 ml. of a liquid culture of the organism to be tested; an equal amount of sterile water was added to the others; and all were thoroughly mixed with a spatula. A worm was left in the inoculated soil for 24 to 72 hours.

TABLE 1

Number of bacteria in soil and in castings of earthworms

INOCULUM	MEDIUM	NO. OF PLATES	COLONIES/GM.	DIFFERENCE IN SOIL POPULATION
			thousands	*per cent*
Sassafras loam	Albumin agar	18	39,110	+14.65
Castings		17	44,820	
Sassafras loam	Albumin agar	18	17,890	
Castings		18	9,500	−46.90
Sassafras loam	Albumin agar	17	12,880	
Castings		17	3,650	−71.66
Sassafras loam	Albumin agar	19	5,740	
Castings		17	9,000	+56.80
Sassafras loam	Albumin agar	18	22,560	
Castings		15	92,670	+310.77
Penn silt loam	Albumin agar	17	18,820	
Castings		12	35,670	+90.38
Penn silt loam	Albumin agar	17	2,120	
Castings		19	1,580	−25.47
Penn silt loam	Albumin agar	16	1,350	
Castings		17	5,940	+340.00
Penn silt loam	Albumin agar	16	17,370	
Castings		13	61,540	+254.29
Sassafras loam	Dextrose-free albumin agar	20	34,500	
Castings		20	2,650	−92.32
Sassafras loam	Dextrose-free albumin agar	20	41,300	
Castings		20	5,500	−86.68
Penn silt loam	Dextrose-free albumin agar	18	55,610	
Castings		20	57,250	+2.95
Penn silt loam	Dextrose-free albumin agar	20	59,450	
Castings		20	15,200	−74.43

The soil in one of the remaining pots was firmed and the worm transferred to it from the pot of inoculated soil. Castings were collected and plated out simultaneously with soil from the inoculated pot and soil from the uninoculated pot.

Number of actinomycetes in soil and in castings of earthworms

INOCULUM	MEDIUM	NO. OF PLATES	COLONIES/GM.	DIFFERENCE IN SOIL POPULATION
			thousands	*per cent*
Sassafras loam	Albumin agar	18	220	
Castings		17	230	+0.45
Sassafras loam	Albumin agar	18	500	
Castings		18	0	∞
Sassafras loam	Albumin agar	17	60	
Castings		17	0	∞
Sassafras loam	Albumin agar	19	260	
Castings		17	1,000	+284.61
Sassafras loam	Albumin agar	18	220	
Castings		15	200	−0.91
Penn silt loam	Albumin agar	17	4,000	
Castings		12	4,170	+4.25
Penn silt loam	Albumin agar	17	1,410	
Castings		19	1,050	−25.53
Penn silt loam	Albumin agar	16	240	
Castings		17	820	+241.66
Penn silt loam	Albumin agar	16	4,060	
Castings		13	5,460	+34.48
Sassafras loam	Dextrose-free albumin agar	19	56	
Castings		19	56	0
Sassafras loam	Dextrose-free albumin agar	20	2,000	
Castings		20	1,000	−50.00
Sassafras loam	Dextrose-free albumin agar	20	400	
Castings		20	350	−12.50
Penn silt loam	Dextrose-free albumin agar	19	2,210	
Castings		20	1,950	−26.70
Penn silt loam	Dextrose-free albumin agar	18	7,350	
Castings		20	8,700	+18.36
Penn silt loam	Dextrose-free albumin agar	20	7,200	
Castings		20	8,300	+15.28
Sassafras loam	Krainsky agar	30	615	
Castings		30	265	−57.72

B. cereus mycoides was counted on plates of nutrient agar and *S. marcescens* on plates of nutrient agar with added traces of ferric and magnesium sulfates for pigment production, with the results shown in tables 5 and 6.

Disappearance of S. marcescens *in the digestive tract*

Because *S. marcescens* was completely extinguished in the digestive tract, it seemed reasonable to suppose that, should the place of its disappearance be located, the reason might be tentatively deduced from a knowledge of the function of the different parts of the tract. The pharynx, the crop, the anterior end of the intestine, and the posterior end of the intestine were selected as strategic points for examining the duct and its contents. The pharynx was chosen to detect the earliest effects of the pharyngeal secretion; the crop, to detect changes that might take place after a longer exposure to the action of the pharyngeal secretion; the upper intestine, to pick up the influence of the gizzard and of prolonged confinement in the digestive tract; and the lower intestine, to show the added effect of all the intestinal enzymes.

TABLE 3

Number of fungi in soil and in castings of earthworms

INOCULUM	MEDIUM	NO. OF PLATES	COLONIES/GM.	DIFFERENCE IN SOIL POPULATION
				per cent
Sassafras loam	Fungus agar	10	29,780	
Castings		10	10,200	−65.75
Penn silt loam	Fungus agar	10	37,500	
Castings		10	31,500	−16.00
Sassafras loam	Fungus agar	10	8,200	
Castings		10	7,400	−9.76
Penn silt loam	Fungus agar	10	45,800	
Castings		10	44,200	−3.49

TABLE 4

Formation of nitrites and nitrates by soil and by castings

INOCULUM	DILUTION FORMING NITRITE	DILUTION NOT FORMING NITRITE	DILUTION FORMING NITRATE	DILUTION NOT FORMING NITRATE
Sassafras loam	1 in 100	1 in 1,000	1 in 100	1 in 1,000
Castings	1 in 10	1 in 100	1 in 1,000	1 in 10,000
Penn silt loam	1 in 500	1 in 1,000	1 in 100	1 in 200
Castings	1 in 500	1 in 1,000	1 in 100	1 in 200
Penn silt loam	1 in 900	1 in 1,000	1 in 200	1 in 300
Castings	1 in 800	1 in 900	1 in 400	1 in 500

Both fresh material and material held for a time in moist sterile vials were examined. Stored samples were included for two reasons: first, to determine whether the disappearance of *S. marcescens* at a given point was the result of something secreted at that point or the result of the continued action of a secretion originating at a more anterior point; second, to bring out, by multiplication in dead tissue, the presence of *S. marcescens* where numbers might be too small to be detected by the same procedure in fresh material.

TABLE 5

Number of mycoides colonies in soil, in inoculated soil, and in castings, developing on nutrient agar

INOCULUM	NO. OF PLATES	COLONIES/GM.	DIFFERENCE IN INOCULATED SOIL POPULATION
		thousands	*per cent*
Sassafras loam	10	0	
Inoc. sassafras loam	10	400	
Castings	10	300	−25.00
Sassafras loam	30	150	
Inoc. sassafras loam	30	300	
Castings	30	115*	−61.67
Penn silt loam	30	115	
Inoc. Penn silt loam	30	1,600	
Castings	30	1,500	−6.25

* This soil was also plated out 19 days later, and about 10 million colonies/gm. were found. Hence, the decrease in the castings was not due to dying out of the inoculum.

TABLE 6

Number of Serratia colonies in soil, in inoculated soil, and in castings, developing on nutrient agar

INOCULUM	NO. OF PLATES	COLONIES/GM.
		thousands
Sassafras loam	10	0
Inoc. sassafras loam	5	4,600
Castings	5	0
Sassafras loam	10	0
Inoc. sassafras loam	10	5,100
Castings	10	0
Sassafras loam	50	0
Inoc. sassafras loam	50	6,750
Castings	50	0

Worms were left for 3 days in a pot of soil that had been inoculated with *S. marcescens* and gave about 12 to 16 million *Serratia* colonies per gram on nutrient agar plates. Upon removal, the worms were washed in tap water and placed, one at a time, in a Petri dish containing enough 30 per cent ethyl alcohol to cover them. As soon as each worm was dead, it was removed from the alcohol, identified, and opened down the middorsal line to expose the digestive tract (fig. 2). The pharynx, the crop, a section of intestine just behind the gizzard, and a section just ahead of the anus were removed and quickly placed in separate, sterile vials containing a few drops of moisture on the bottom. Each organ or segment was then macerated and the contents were squeezed out with sterile forceps. The vials were plugged with cotton and held in a covered water bath. Dilutions of the resulting pulp were made by transferring two loopfuls into water blanks, which were further diluted. As inocula for plates of nutrient agar with added ferric and magnesium sulfates, 1 ml. portions of selected dilutions were used. Similar dilutions were made after 24 and 48 hours, and all plates were examined for the presence of *S. marcescens* after 4 or 5 days.

TABLE 7

Number of S. marsescens colonies in undiluted pharyngeal and crop contents of earthworms

INOCULUM	PLATE NO.				
	1	2	3	4	5
Worm 1, pharynx	3	3	2	2	2
Worm 1, crop	0	1	2	0	0
Worm 2, pharynx	0	1	0	1	0
Worm 2, crop	0	0	0	0	0
Worm 3, pharynx	0	0	0	2	0
Worm 3, crop	0	0	0	0	0

Plates inoculated with fresh material showed few colonies from the pharynx and crop, numerous colonies from the upper and lower intestine, and no *Serratia* at any point. After storage for 24 hours, numerous colonies developed from all four parts of the digestive tract; *S. marcescens* colonies appeared from pharynx inocula but not from crop or intestine. Three repetitions with different worms gave identical results. The repeated development of *S. marcescens* in the pharynx during storage of the dead tissue suggested that its presence might be uncovered in fresh material if sufficiently low dilutions were used. Accordingly, the experiment was repeated with three worms, five plates being streaked directly with a platinum loop which had been inserted into the cavity of the pharynx or crop. The crops of all three worms were filled and distended with soil, whereas the pharynx appeared to be empty. The growth on the plates (table 7) proved that *S. marcescens* was present in the pharynx in small numbers, in spite of its apparent lack of contents, but *S. marcescens* could not be demonstrated in the soil-filled crop in two out of three cases.

DISCUSSION

The results on total numbers obtained from fresh castings do not confirm Heymons' (11) designation of the worm intestine as a breeding place for bacteria generally. It is obvious that, though striking increases and decreases take place in some instances, *L. terrestris* does not exert any consistent influence on the total population of soil while it is in the worm. Different soils and the same soil at different times might be expected to contain different proportions of resistant and susceptible groups of bacteria. The findings on nitrifying bacteria in no way contradict the belief, so often stated since Keller, that nitrification is especially strong in earthworm excreta. They indicate rather that such nitrification as occurs must be due to the environment of the castings rather than to any increase in nitrifying bacteria within the worm.

The fact that *S. marcescens* died out completely in the digestive tract cannot be used as a basis for generalizing about gram-negative, non-spore-forming bacteria. Still it would be strange if some other species do not behave in the same way. On the other hand, finding gram-negative, non-spore-forming bacteria in excreta would not be evidence that they were soil organisms which had passed through the digestive system and retained viability. Although Bassalik isolated numerous organisms from the earthworm intestine, there is no proof of an indigenous intestinal flora for *L. terrestris*. Yet it is reasonable to suppose that one exists, and these organisms would naturally appear in the excreta.

The manner in which *B. cereus mycoides* persists, but in generally reduced numbers, permits one to surmise that more or less destruction of vegetative cells may take place while spores survive.

In four out of five worms, *S. marcescens* cells were killed at some point anterior to the crop; in all five worms, destruction took place before the ingested soil reached the upper end of the intestine. This suggests that the killing agent may be the secretion of the pharyngeal glands acting during the short time it takes soil to pass from the pharynx to the crop. It would be just as reasonable from these findings to postulate a killing agent in the esophagus or in the crop, but no digestive secretions have been demonstrated for these organs. Robertson (18) showed the secretions of the calciferous glands to be inactive in neutralization, and the crop is regarded generally as a mere storage organ.

SUMMARY AND CONCLUSIONS

The total numbers of bacteria, actinomycetes, and fungi are not consistently greater or less in fresh castings of *L. terrestris* than in soil.

Nitrifying bacteria do not undergo any important increase or decrease while passing through the earthworm.

B. cereus mycoides undergoes some reduction of numbers in the earthworm.

S. marcescens is killed out completely, apparently by the action of the pharyngeal secretion.

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EFFECTS OF AUTOCLAVINGS UPON THE 10-YEAR OUTGO OF NUTRIENTS FROM CUMBERLAND SILT LOAM

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The results of heat treatments of soil upon seed germination and plant growth have been reported by a number of investigators since 1907 (1, 5, 6, 9, 10, 11, 12, 13, 14).

In 1912, Schreiner and Lathrop (15) reported upon the chemistry of steam-heated soils, with particular reference to the development of organics, such as dihydroxystearic acid. The effects of heat treatments upon the forms and extractability of manganese in soil were studied by Kelly and McGeorge (7), Conner (2), McCool (8), and by Fujimoto and Sherman (3, 4).

The primary objective of steaming beds for tobacco seeding has been to diminish effects of fungi and to kill weed seeds. In some instances, however, in the foregoing citations, heat treatments were found to have induced favorable chemical and biochemical transitions, as measured through extractions, whereas opposite effects resulted in other cases. So far as known to the authors of this paper, the early and the protracted effects of single and successive steamings upon dissolubility of soil nutrients have not been determined through the leaching action of rain water over a period of years. The findings reported here were obtained through a 10-year lysimeter study, in which the leachability of the cations and anions served to register the effects of various autoclavings of a soil that is used extensively in obtaining seedlings of Burley tobacco in Eastern Tennessee. It was assumed that an autoclaving would be the equivalent of a thorough steaming that would be imposed in practice.

EXPERIMENTAL METHODS

The soil used was Cumberland silt loam. It had been limestoned a year previously and had been in bluegrass pasture for at least 30 years. Hence, it had acquired a good supply of organic matter and substantial fractions of its contents of Ca, Mg, K, and possibly Na, were expected to be in an exchangeable state. Partial analysis of the untreated soil showed N, S, carbonate-CO_2, CaO, and MgO contents of 0.124, 0.025, 0.190, 0.635, and 0.504 per cent respectively; pH 7.7; and exchangeable Ca, Mg, K, and Na contents of 9.42, 2.10, 0.18, and 0.15 me. per 100 gm. respectively.

The over-all bulk of well-mixed soil was screened, while in good condition as to moisture content, and then was divided into 100-pound portions, moisture-free basis. The several portions then were subjected to the following autoclavings, each of which was of 1-hour duration at 20-pound build-up pressure after the charge had been brought to the critical temperature:

No autoclaving: nine annual workings of soil.
Single autoclaving: nine annual workings of soil.

Two successive *annual* autoclavings: nine annual workings of soil.
Three successive annual autoclavings: nine annual workings of soil.
Three autoclavings at 1-day intervals: soil undisturbed throughout 10 years.
No autoclaving: soil undisturbed throughout 10 years.

Each 100-pound charge of autoclaved soil and of the unsteamed controls was placed in a 1/20,000-acre imbedded lysimeter and exposed to rain-water leachings by the 10 annual precipitations recorded in chronological order in the footnote to table 2. A definite fraction of every periodic collection of the leachings from every lysimeter was reserved to provide a composite for analysis. The volumes of the leachings from each lysimeter and quantities of nutrents leached per annum, and as 10-year totals, are given in tables 2 and 3.

TABLE 1

Outgo of nitrogen in ammoniacal, albuminoid, and nitrate forms from autoclaved soils during the initial year[*]

AUTOCLAVINGS	POUNDS N PER 2,000,000 POUNDS OF SOIL					
	Ammoniacal		Albuminoid		Nitrate	
	First Leaching[†]	Total	First Leaching[†]	Total	First Leaching[†]	Total
None	0.41	0.52	0.41	0.62	87.5	137.1
One	0.51	0.69	2.83	3.19	118.6	158.3
Two[#]	0.53	0.72	2.72	3.10	116.0	139.8
Three[#]	0.51	0.78	2.59	3.03	104.7	128.9
Three[‡]	1.19	1.60	4.74	6.85	100.8	121.7
None	0.22	0.33	0.44	0.66	76.0	115.6

[*] Annual rainfall of 35.7 inches; average leaching, 14.4 inches, or 40.3 per cent of rainfall.
[†] All leachings from the steamed soils were yellowish.
[#] Successive years.
[‡] On successive days.

LEACHINGS

Nitrogen outgo

During the initial year all of the periodically collected leachings were analyzed for their contents of nitrogen in ammoniacal, albuminoid, nitrite, and nitrate forms. The respective quantities in the first leachings and totals for all of the leachings collected throughout the initial year are given in table 1. During the first year every collection from every autoclaved soil was yellowish brown, because of dissolved organic matter. The outgo in each of the forms reported was carried chiefly by the initial leachings that occurred between placement, July 31, and December 18. In every instance, however, nitrites were virtually absent. The leachings obtained during the second year were colorless and were found to be devoid of nitrogen in forms other than nitrate.

Although the initial leachings of nitrates were decidedly greater from the autoclaved soils than from the untreated soils, the first-year totals were not very different.

TABLE 2

The 10-year effects of single and replicated autoclavings of Cumberland silt loam, as registered by rain water leachings of nitrates and sulfates

YEAR	NO. STEAMING, ANNUAL WORKING	SINGLE STEAMING, ANNUAL WORKING	TWO ANNUAL STEAMINGS, ANNUAL WORKING	THREE ANNUAL STEAMINGS, ANNUAL WORKING	THREE DAILY STEAMINGS, UNDISTURBED THEREAFTER	NO STEAMING, UNDISTURBED
Liters leached per lysimeter						
1st........	70.3	72.9	75.2	72.5	77.0	75.3
2nd.......	128.7	143.7	158.5	152.8	151.3	140.9
3rd.......	148.2	153.2	161.1	159.5	158.4	159.0
4th.......	74.0	77.5	82.1	82.5	75.9	74.9
5th.......	140.6	147.4	158.5	155.0	141.2	148.5
6th.......	167.7	168.0	173.2	169.2	164.9	169.7
7th.......	110.0	108.9	118.2	114.5	113.1	116.4
8th.......	133.0	136.4	147.0	142.0	139.0	143.6
9th.......	165.3	159.3	165.5	162.4	165.8	166.5
10th.......	72.4	67.1	75.7	73.8	72.1	73.5
Total....	1210.0	1234.0	1315.0	1284.0	1259.0	1268.0
*Nitrogen leached—pounds of N per acre**						
1st........	137	158	140	129	122	116
2nd........	123	120	148	137	105	97
3rd.......	87	72	78	90	45	60
4th.......	62	60	48	56	57	83
5th.......	47	49	47	36	53	60
6th.......	58	44	49	38	52	59
7th.......	43	37	43	32	39	40
8th.......	28	29	28	29	33	30
9th.......	20	26	25	29	29	24
10th.......	23	24	21	20	23	14
Total.....	628	619	627	596	558	590
*Sulfur leached—pounds of SO_3 per acre**						
1st........	143	176	181	174	200	138†
2nd.......	139	191	175	174	131	129
3rd.......	106	137	114	123	96	95
4th.......	101	107	93	104	90	108
5th.......	107	100	94	93	116	111
6th.......	115	109	108	104	116	109
7th.......	94	92	98	95	91	93
8th.......	104	109	97	101	104	96
9th.......	88	107	101	106	105	98
10th.......	116	101	96	98	95	92
Total....	1,113	1,229	1,157	1,172	1,144	1,069

* Pounds per 2,000,000 pounds of soil.

† Total increment of 1,115 pounds through rain waters.

Successive annual rainfall, inches: 35.7, 58.3, 55.95, 50.61, 58.30, 48.50, 63.58, 56.30, 34.18, 48.03, total 509.45.

TABLE 3

The 10-year effects of a single and replicated autoclavings of Cumberland silt loam as registered by rain-water leachings of calcium, magnesium, and potassium

YEAR	NO STEAMING, ANNUAL WORKING	SINGLE STEAMING, ANNUAL WORKING	TWO ANNUAL STEAMINGS, ANNUAL WORKING	THREE ANNUAL STEAMINGS, ANNUAL WORKING	THREE DAILY STEAMINGS, UNDISTURBED THEREAFTER	NO STEAMING, UNDISTURBED
Calcium leached—pounds $CaCO_3$ per acre[*][†]						
1st........	907	974	1,000	950	1,018	923
2nd.......	1,116	1,194	1,391	1,266	1,159	1,124
3rd.......	1,080	983	1,009	1,185	863	1,041
4th.......	582	592	537	565	553	661
5th.......	832	749	799	727	798	892
6th.......	793	753	811	730	792	857
7th.......	626	543	618	557	613	626
8th.......	776	674	760	683	687	703
9th.......	695	658	644	649	656	688
10th.......	486	443	430	426	425	401
Total....	7,893	7,563	7,999	7,738	7,564	7,916
Magnesium leached—pounds $MgCO_3$ per acre[*][‡]						
1st........	81	52	54	51	45	81
2nd.......	75	64	64	54	64	86
3rd.......	78	59	57	50	47	78
4th.......	39	29	25	23	25	41
5th.......	51	54	60	46	46	66
6th.......	62	52	51	48	52	64
7th.......	38	28	33	25	31	37
8th.......	52	41	50	42	42	47
9th.......	62	53	51	47	51	56
10th.......	38	30	30	28	28	29
Total....	576	462	475	414	431	585
Potassium leached—pounds K per acre[*][§]						
1st........	12	20	19	23	18	10
2nd.......	4	11	15	15	16	16
3rd.......	5	10	11	11	11	4
4th.......	2	4	5	6	5	2
5th.......	3	9	13	11	11	5
6th.......	4	7	8	8	10	6
7th.......	2	6	6	6	6	3
8th.......	5	7	9	8	7	5
9th.......	8	10	10	9	10	4
10th.......	2	3	4	3	3	2
Total....	44	87	100	100	97	47

[*] Per 2,000,000 pounds of soil.

[†] Total increment of 798 pounds through rain waters.

[‡] Total increment of 350 pounds through rain waters.

[§] Total increment of 122 pounds through rain waters.

Because of the cited effects of steamings upon the manganese content of the soil (2, 3, 4, 7, 8), it was thought that the observed brownish coloration of the lysimeter leachings during the initial year might be due to dispersed hydrated oxides of manganese. The assumption was disproved, however, through hydrogen peroxide destruction of the coloration of the residues from the evaporated leachings.

After the first year, nitrogen outgo was solely in the form of nitrates. Table 2 shows that large amounts of nitrogen were leached from all the soils during the first 2 years, but presents no conclusive evidence as to effects of the steamings. Thereafter, all nitrate leachings were substantially less, without consistent indication that the various steam-treatments had influenced nitrification significantly during the remainder of the 10 years. In no case, however, did heat treatment increase the 10-year total outgo of nitrogen.

Sulfate outgo

All of the steam treatments induced increases in sulfate outgo during the first year, whereas the initially imposed triple autoclaving reduced the sulfate leachings during the second year. Although every comparison registered a larger overall outgo of sulfates from the steamed soil, largest SO_3 outgo was only 116 pounds greater than that from the corresponding control soil, and neither of the controls yielded sulfates equal to the increments derived from the rainwaters.

Calcium outgo

Every steam treatment induced some increase in the amount of calcium leached during the first 2 years, when the nitrate leachings were highest. Moreover, in three of the four comparisons between the outgo of calcium from the autoclaved soils and from the respective controls, the unsteamed soil gave the larger total leaching of that element and this parallels the 10-year leachings of nitrogen. The quantity of calcium brought down in the rainwaters was only 10 per cent of the mean over-all outgo of that element.

Magnesium outgo

The effect of the steamings upon the leachings of magnesium during the first 2 years was opposite to the effect found for calcium. In nine of the ten annual leachings, outgo of magnesium from the repeated annual steamings and annual workings was less than the outgo from the unsteamed and annually worked soil. Moreover, every annual outgo of magnesium from the thrice-steamed and unworked soil was less than the amount that passed from the unsteamed and unworked control, with a resultant over-all disparity of 24 per cent in the outgo of that element.

Potassium outgo

The annual steamings substantially enhanced the leachings of potassium during the first 3 years, although the accelerative effect was not furthered by the third annual steaming. In every comparison, the enhancement in outgo of K was evidenced through the annual passages, and every comparison showed that steaming served to increase greatly the over-all outgo of that element. In 9 of the 10 years, such increases from the thrice-steamed unworked soil resulted in doubling the 10-year total outgo of K. It will be noted, however, that no outgo of K was as large as the increment supplied by the 10-year rainfall at Knoxville, where soft coal usage is high.

Sodium outgo

Although it was assumed that the soil had a meager content of sodium, the leachings of that element from the variously steamed soils were determined at the end of the first year. Then it was learned that the outgo of sodium was substantially greater than the outgo of potassium. The initial content of exchangeable sodium was determined at the end of the experiment and was found to be almost equal to the corresponding content of potassium. It is not known to what extent the larger leaching of sodium was from increments brought by rain waters and from previous topdressings of nitrate of soda in the development of pasture.

The increases in the outgo of sodium induced by the single steaming and by the repetitive steamings were comparable and larger than the increase of only 2 pounds that was registered by the triplicate day-to-day steamings. The difference probably is not significant. Since distinctive differences in the outgo of sodium during the first year were not registered by variations in the steamings, and since it had been found that leachings of that element seldom extend beyond the initial annual period, determinations of sodium outgo were not made after the first year.

SUMMARY AND CONCLUSIONS

Since the steaming of soils is advocated as an effective procedure for eradicating fungi and nematodes from tobacco-bed soils and for killing weed seeds, a 10-year lysimeter study was conducted to ascertain the effects of autoclave steamings upon immediate and subsequent availability of soil nutrients. Cumberland silt loam was subjected to 1, 2, and 3 annual autoclavings and attendant annual workings, and to three day-to-day steamings initially with appropriate unsteamed controls, and the rain-water leachings of soil nutrients were determined annually.

The effects of the steamings upon the solubility of soil organic matter were indicated by the brownish coloration of the early leachings and by their content of ammoniacal and albuminoid forms of nitrogen, without occurrence of nitrites. Large quantities of nitrates passed from the steamed and from the unsteamed soils during the first 2 years without indication that the various steamings had induced significant changes in nitrification, although the steamings effected slight decreases in the 10-year totals for nitrate outgo.

An accelerative effect of steaming upon sulfate outgo was registered during the first 3 years and some increases were shown for the 10-year duration.

Calcium outgo was increased by the steamings through the first 2 years, but not thereafter and, with one exception, the 10-year outgo of calcium from every steamed soil was less than the total quantity that passed from its resp ectiv control.

Conversely, magnesium outgo was lessened by the steamings, both initially and throughout the 10 years.

In contrast, potassium outgo from the steamed soils was accelerated greatly, during the first 3 years in particular, and the several outgo totals were double those that passed from the corresponding controls.

The several steaming procedures induced relatively small increases in sodium leachings during the first year, the outgo being substantially greater than the outgo of potassium.

As an over-all conclusion, it appears that beneficial effects of the steam treatment of tobacco-bed soils should be attributed solely to the inactivation of fungi and to the killing of weed seeds, rather than to increases in the supply of nutrients, with the single exception of potassium.

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INFLUENCE OF SEASONAL AND CULTURAL CONDITIONS ON AGGREGATION OF HAGERSTOWN SOIL[1]

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Soil structure is becoming a factor of increasing interest and concern as its effects on runoff and erosion, land capability, and plant growth are more fully appreciated. For this reason, there is need for much more information than is now available concerning the maintenance and improvement of the structural condition of a given soil in a particular environment and concerning factors that affect soil aggregation and structure.

The purpose of this investigation was to study the influence of seasonal as well as cultural conditions on the aggregation of Hagerstown soil in central Pennsylvania.

Seasonal variability in the aggregation of different soil types has been reported by several investigators (1, 5, 7). In some instances consideration was given to possible reasons for differences in the aggregation of the particular soil type at various periods during the year. The effects of various management practices on soil structure have been reported by numerous investigators.

PLOT DESCRIPTION AND TREATMENT

Aggregation and moisture content at 25 different sampling dates were determined on samples taken from the mulch and soil amendment experimental plots at the Pennsylvania Agricultural Experiment Station from March 1944 to March 1946. These plots and results of the first year's study were described in a previous publication (1). Corn was grown on the plots during both years. During the second year, for comparison the soil beneath a 5-year-old Kentucky bluegrass sod border area separating the plots was sampled, along with that from a 65-year old bluegrass sod border separating plots 15 and 16 in Tier I of the Jordan soil fertility experiment.

During the third and fourth year, May 1947 to May 1949, the soil from six $\frac{1}{10}$-acre runoff plots on Hagerstown silty clay loam at the Soil Conservation Experiment Station was sampled at 24 different dates. These plots are included in a study of the effect of different fertilization practices on runoff and erosion. A 4-year corn-oats-wheat-hay rotation is used in which the following treatments are applied in duplicate: (*a*) barnyard manure plowed down with the red-clover–timothy-hay sod at the rate of 8 tons per acre; superphosphate applied in the row to the corn and wheat at the rate of 200 pounds per acre; (*b*) a complete fertilizer (4-12-4) applied in the row to the corn, oats, and wheat at the rate of 250 pounds per acre; (*c*) no fertilizer treatment. Lime is applied to each plot at the rate of 1 ton of limestone per acre prior to fall plowing for wheat. These plots were in corn in 1947 and in oats in 1948.

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[1] Cooperative contribution of the department of agronomy, Pennsylvania Agricultural Experiment Station, and the Soil Conservation Service, U. S. Department of Agriculture, State College, Pa. Paper 1546 in the Journal Series of the Pennsylvania Agricultural Experiment Station. The valuable assistance of James A. Cook of the Agronomy department in the sampling and analytical operations is gratefully acknowledged.

EXPERIMENTAL PROCEDURE

The sampling procedure and the wet-sieve method of aggregate analysis of the soil in its field moist condition were the same as those described in a previous publication (1) except that from each of the larger runoff plots eight separate samples were taken at each date and composited for analysis.

The structural condition of the soil at a given moisture content was expressed as the percentage of the soil which consisted of aggregates and of primary particles > 0.25 mm. in diameter. The content of primary particles was uniform in the soil from the different plots, thus eliminating the possibility of apparent differences in structure due to such variability.

Daily precipitation records were obtained with the standard 8-inch U. S. Weather Bureau rain and snow gage.

Mean daily soil temperature readings were obtained with an automatically recording soil thermograph. Three-day mean temperatures were determined by averaging the mean daily temperatures for successive 3-day periods throughout the month. The temperature at the 3-inch depth in bluegrass sod, adjacent to the experimental plots, was taken to represent the mean daily temperature of the 0–6-inch surface soil layer.

To determine the effect of different moisture contents on the water-stable aggregation of Hagerstown silty clay loam under different treatments at a particular time during the growing season, large composite samples were taken from each of the runoff plots on June 10, 1948. These samples were placed in a 2-inch layer on large trays with fine wire bottoms and slowly moistened to near saturation with a low pressure atomizer-type sprayer. Samples were carefully taken from the soil at maximum water-holding capacity. During slow drying, samples for aggregate analysis and moisture content were taken at 48-hour intervals until the air-dry condition was reached. Air-dry samples were then oven-dried at 105°C. to determine the effect of this treatment on aggregation. To determine the effect of rewetting the air-dried soil to moisture contents approximating those of samples taken during slow drying, six 300-gm. samples of each of the differently treated soils were spread in very thin layers and moistened to the appropriate degree with the atomizer-type sprayer.

Immediately after each sampling, the soil was placed in an excess of distilled water and allowed to slake for 24 hours. The >0.25-mm. fraction was then separated by wet sieving. This is a departure from the usual pretreatment procedure, in which the soil is allowed to air-dry before it is placed in an excess of water for fractionation of the sample. The conventional method of aggregate analysis measures what might be considered the residual water-stable aggregation after the soil is dried to some more or less definite moisture content. In this study an attempt was made to determine the percentage of water-stable aggregates in the soil under field conditions, wherein moisture content and to a lesser degree temperature appeared to exert a very pronounced influence at any given period throughout the year.

EXPERIMENTAL RESULTS

The effects of variation in seasonal conditions on aggregation of Hagerstown silt loam from the mulch and soil amendment experimental plots for the 1-year period, March 1944 to March 1945 are presented in figure 1. Findings for the succeeding year, in which were included the figures for soils under 5- and 65-year-old bluegrass sods, are presented in figure 2. The mean soil temperatures at a depth of 3 inches for 3-day periods throughout the year were included as supplementary information, of particular importance in analyzing the effect of winter conditions on soil aggregation.

Throughout the first year the soil aggregation curve paralleled the soil moisture curve with only a few exceptions. The soil temperature and soil aggregation curves evidenced an inverse relationship for this particular year. Water-stable aggregation was at a minimum during July and August when soil moisture was lowest and reached its maximum following 2 months of continuous freezing at a moisture content slightly above field capacity. The effects of freezing upon water-stable aggregation, however, proved to be only temporary.

During the next 12-month period, March 1945 to 1946, the effect of moisture content on water-stable aggregation was strikingly demonstrated. This relationship, under summer conditions, is illustrated in the data for August 24, where, within a 24-hour period following a gentle 0.75-inch rain, the aggregation of this soil was increased approximately 35 per cent.

On the other hand, high soil moisture content accompanied by repeated freezing and thawing during the winter of 1945–46, as shown by the wide fluccuations in 3-day mean soil temperatures (fig. 2), resulted in fluctuations in aggregation. Water-stable aggregation of the soil, following a winter such as this, was lower than that following a winter such as the previous one in which the soil remained frozen beneath a snow cover for 3 months. The aggregation of the soil that had been in Kentucky bluegrass sod for 5 and 65 years also varied from season to season. Bluegrass has brought about a very marked improvement in aggregation after 5 years when compared with that of the cultivated plots.

The aggregation and moisture content of the soil runoff plots during the 1947 and 1948 growing seasons showed a striking association, which is illustrated in figures 3 and 4. The effects on water-stable aggregation of different winter conditions that prevailed in 1947–48 and in 1948–49 are again demonstrated in this 2-year study.

The effect of different fertilization practices in a corn-oats-wheat-hay rotation on the water-stable aggregation of the soil during the fifth and sixth years in which these treatments have been maintained are also shown in figures 3 and 4. Both the manure-phosphate and the complete fertilizer treatments have maintained a higher percentage aggregation than that in the unfertilized plots. No

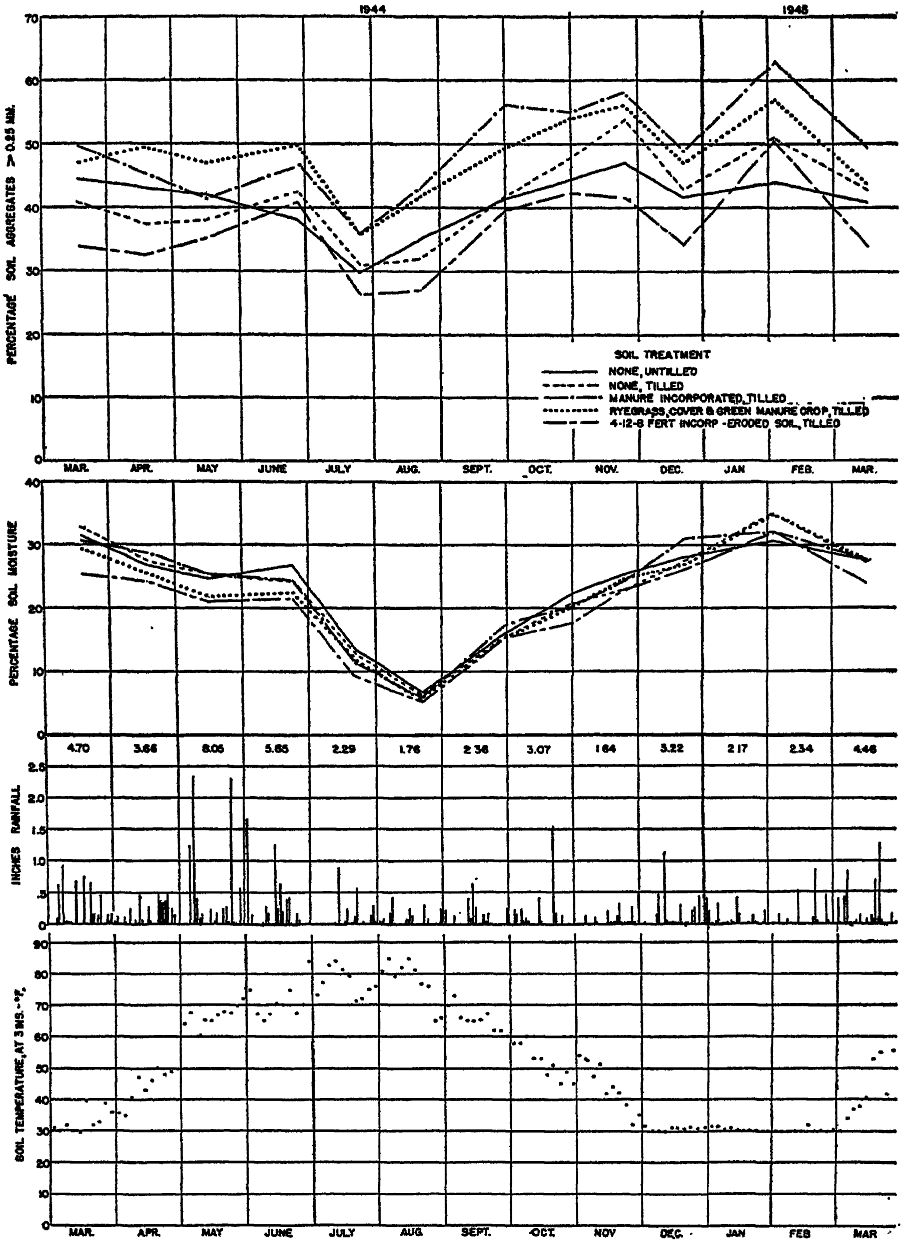

FIG. 1. SEASONAL EFFECTS ON AGGREGATION, MOISTUTE CONTENT, AND TEMPERATURE OF HAGERSTOWN SILT LOAM SURFACE SOIL UNDER VARIOUS TREATMENTS FROM MARCH 1944 TO MARCH 1945

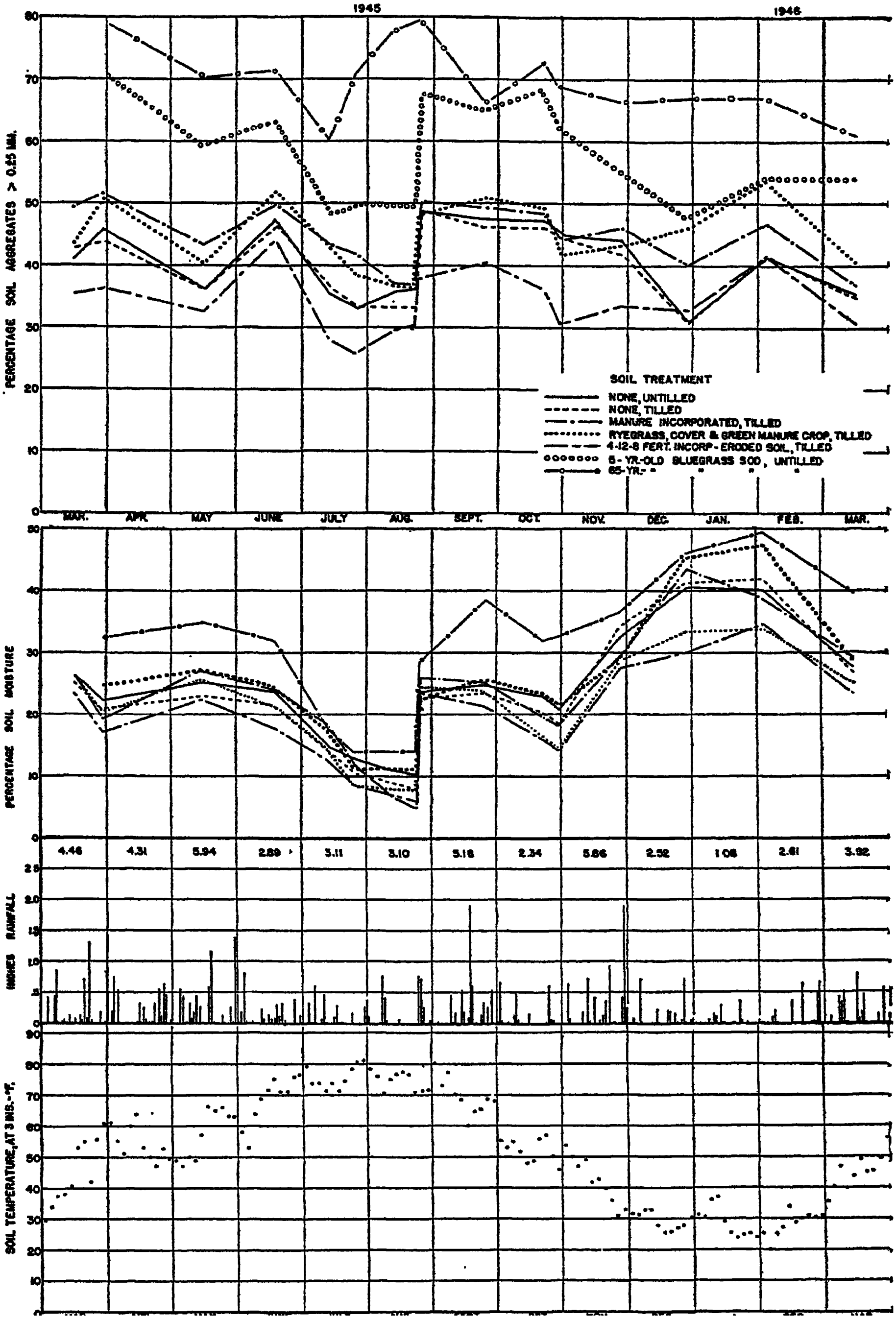

Fig. 2. Seasonal Effects on Aggregation, Moisture Content, and Temperature of Hagerstown Silt Loam Surface Soil Under Various Treatments from March 1945 to March 1946

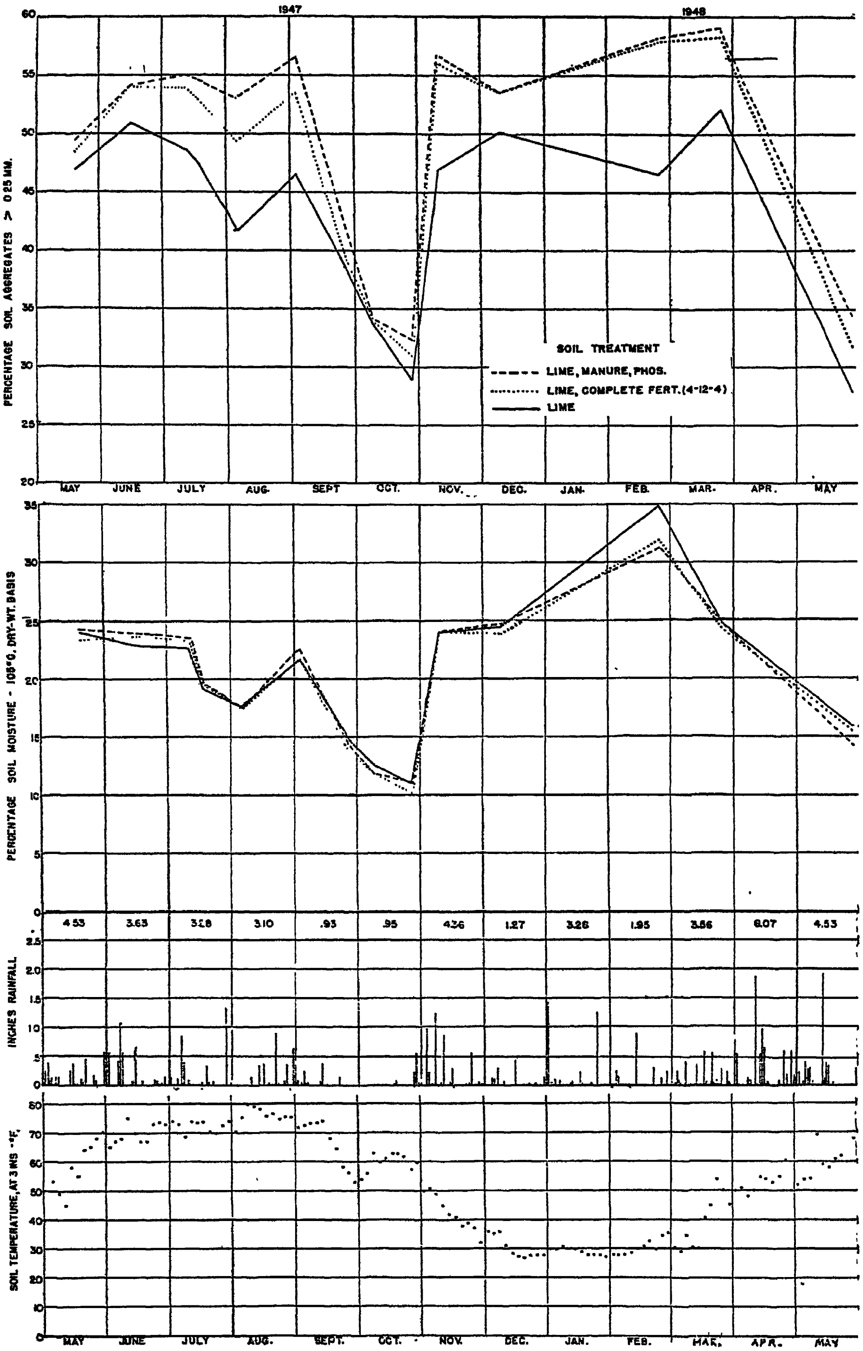

FIG. 3. SEASONAL EFFECTS ON AGGREGATION, MOISTURE CONTENT, AND TEMPERATURE OF HAGERSTOWN SILTY CLAY LOAM SURFACE SOIL UNDER VARIOUS TREATMENTS FROM MAY 1947 TO MAY 1948

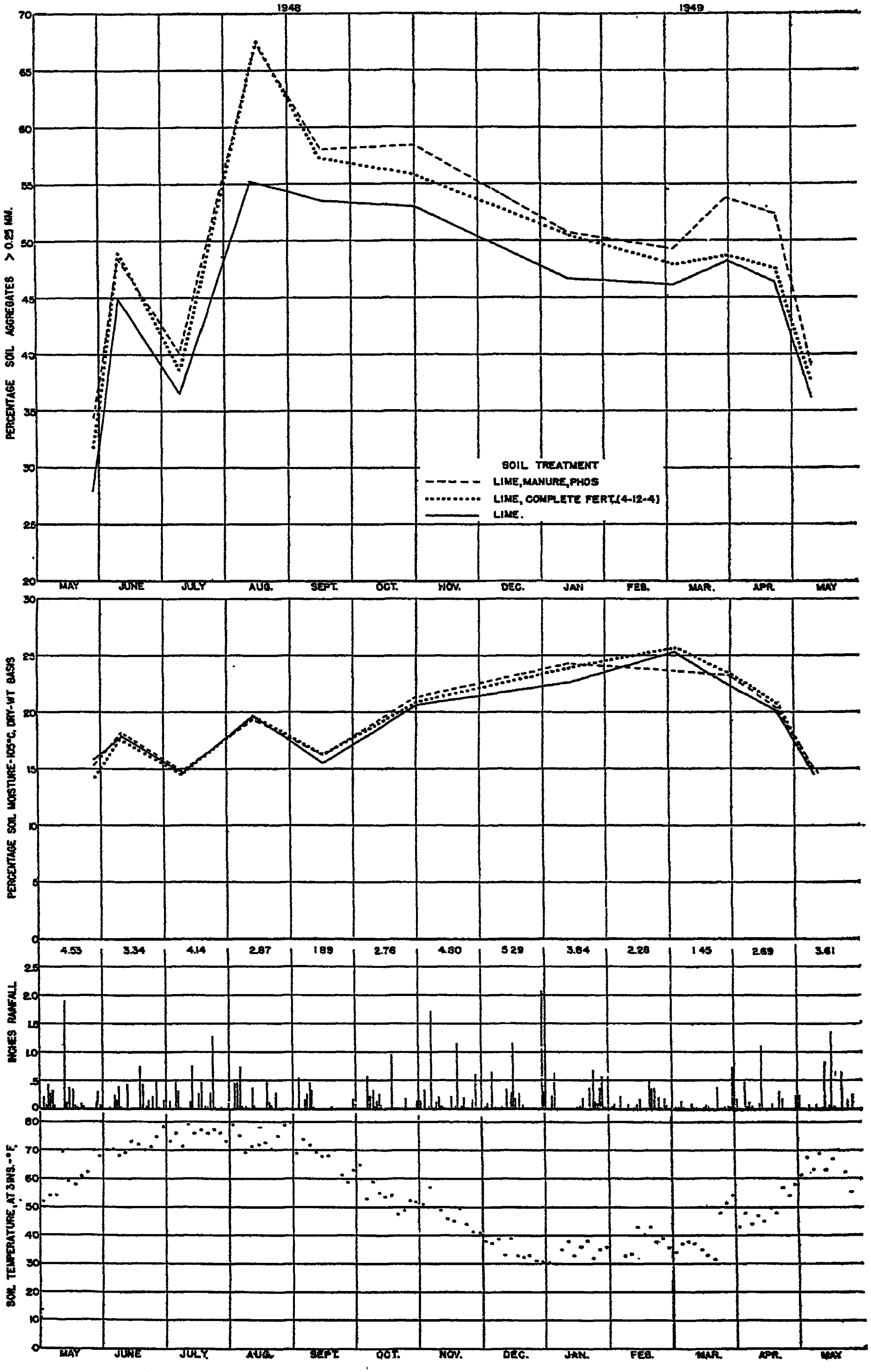

FIG. 4. SEASONAL EFFECTS ON AGGREGATION, MOISTURE CONTENT, AND TEMPERATURE OF HAGERSTOWN SILTY CLAY LOAM SURFACE SOIL UNDER VARIOUS TREATMENTS FROM MAY 1948 TO MAY 1949

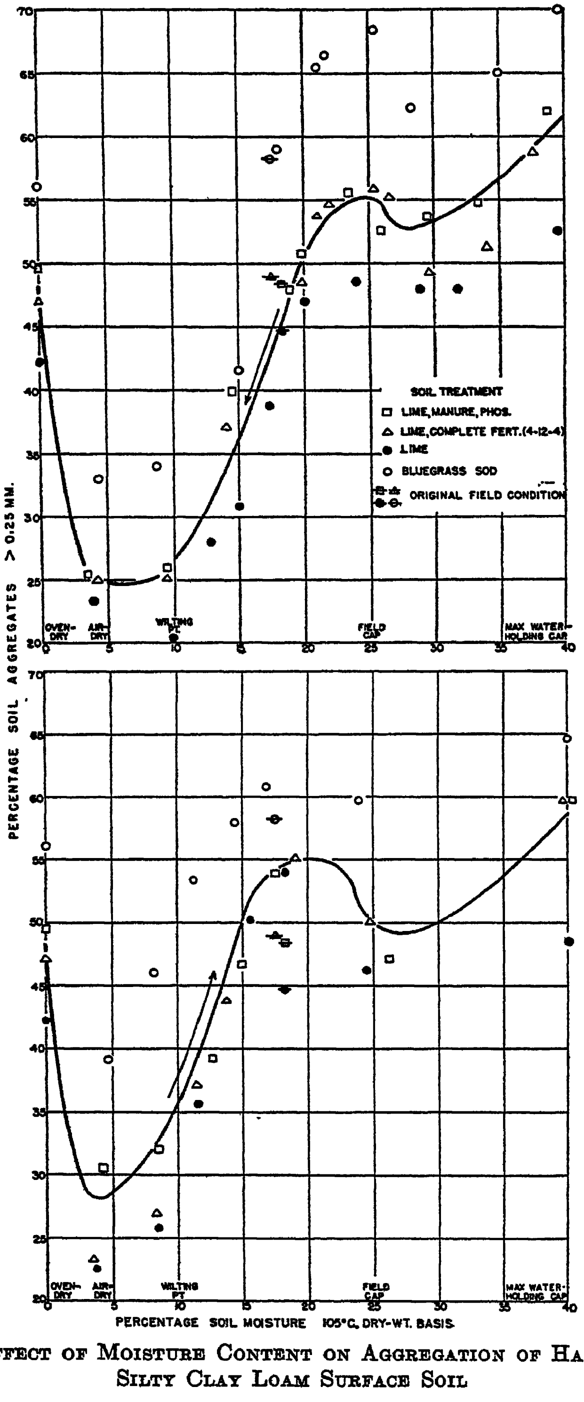

FIG. 5. EFFECT OF MOISTURE CONTENT ON AGGREGATION OF HAGERSTOWN SILTY CLAY LOAM SURFACE SOIL

appreciable difference in the effect of the two fertilization treatments, however, became evident during the period of this investigation.

The effects of different moisture contents on the water-stable aggregation of Hagerstown silty clay loam are shown in figure 5. Aggregation of this soil, at moisture contents ranging from maximum water-holding capacity to oven-dryness, as it was dried or wetted to either one of these extremes exhibited marked variations. Between field capacity and air-dryness, moisture content exerts a very pronounced effect on the percentage of the soil consisting of water-stable aggregates > 0.25 mm. in diameter. Removal of the 3 to 5 per cent moisture contained in the soil at air-dryness, by oven-drying at 105°C. for 24 hours, resulted in a very abrupt increase in aggregation. Aggregation decreased at moisture contents immediately above field capacity, but as maximum water-holding capacity was approached, aggregation reached a maximum for this soil. Wetting this soil to maximum water-holding capacity and then allowing it to dry slowly to its original moisture content at the time it was removed from the field had no effect on its aggregation. Allowing the soil to air-dry and then wetting it effected an increase in macoaggregation over that at the original field-moisture condition. The manner in which the soil is moistened has been shown to have an important effect on the amount of aggregation measured (9).

DISCUSSION

Results of this 4-year investigation on the aggregation of two types of Hagerstown soil show that effects of seasonal differences may be as great as or considerably greater than effects of various soil treatments.

Although a great many other factors undoubtedly influence the aggregation of a given soil at the time of sampling, soil moisture content appears to have the greatest immediate effect on the amount of soil aggregated into the larger water-stable secondary particles or macroaggregates having diameters > 0.25 mm. This has been observed and measured by numerous investigators (1, 2, 3, 5, 6, 8, 9, 11).

Soil temperature-moisture conditions that occur during winter constitute an important seasonal influence on aggregation. Continuous freezing resulted in an increase in aggregation. Intermittent freezing and thawing effected a decrease in aggregation. The degree of aggregation at the end of each winter is temporary, being subject to alteration very early in spring.

The effect of moisture on soil aggregation, as shown in figure 5, suggests the importance of maintaining an adequate supply of moisture in the soil not only as a direct necessity for plant growth but also in view of its possible indirect influence. That plants grow best when the soil contains an adequate supply of moisture may be partly due to an increased amount of soil aggregated into larger sized secondary particles which should provide greater permeability to both air and water. That the greatest runoff and erosion losses generally occur from clean-tilled crops during the hot, dry summer months is no doubt attributable, in part at least, to the decreased number of large water-stable aggregates as the moisture content of the soil approaches the air-dry condition. It is this condition that frequently exists at the surface of the soil during summer. During periods of intense rainfall, this air-dry surface layer is rapidly wetted if left exposed to the direct impact of raindrops. Under these conditions, the water-stability of the larger aggregates in the soil is at a minimum, resulting in formation of the familiar surface crust, characterized by a high percentage of aggregates of silt and fine sand size, which impart to this layer its low infiltration capacity and general impenetrability to air as well as to newly germinated seedlings. If the soil surface is protected by a mulch or a vegetative canopy, wetting takes place less rapidly, allowing the soil to moisten slowly, thus approaching that degree of aggregation which the soil will attain at field capacity. This accounts, in part, for the importance of surface protection in soil and water conservation (4). It may also be important in connection with supplemental irrigation.

The influence of different cultural conditions on the aggregation of Hagerstown silt loam throughout the year, as shown in figures 1 and 2, is reflected first in the manner in which both the manure and annual ryegrass cover crop treatments have maintained a higher level of aggregation than that in the untreated control plots. In the eroded condition, wherein only half of the prevailing organic matter content of this soil remained, aggregation was also decreased. Apparently the greatest rate of improvement in aggregation under Kentucky bluegrass sod occurred within the first 5 years.

The results of the study of different fertility treatments on the aggregation of Hagerstown silty clay loam show that while corn, oats, and wheat occupied the ground in a 4-year rotation, both the manure-phosphate-lime and the complete fertilizer-lime treatments improved the aggregation.

The differences in aggregation attributable to different treatments of this soil remain consistent throughout the year and also appear to be independent of the moisture content at which the soil is analyzed. When each seasonal sample was air-dried to a uniform moisture content prior to aggregate analysis (1), water-stable aggregation in this soil was at a maximum during summer and at a minimum during winter, a finding which is in general agreement with those of Henin (5). Slater and Hopp (10) have also reported that freezing and thawing brought about a decrease in water-stability of their soils, which were air-dried prior to analysis.

SUMMARY

Structural studies of two types of Hagerstown surface soil over a 4-year period have shown that seasonal and cultural conditions are capable of exerting a very pronounced influence on the percentage of soil aggregated into particles > 0.25 mm.

Soil moisture content during the growing season has a marked effect on the water-stable aggregation in soil of these types. The duration and the manner of freezing and the moisture content of the soil also affect aggregation during winter, although this effect was found to be very temporary. Seasonal conditions caused a variation in the aggregation of this soil under all types of treatment. Significant treatment differences in aggregation persisted throughout the year, irrespective of the actual amount of soil aggregated under a particular treatment at any given sampling period. After 5 years in Kentucky bluegrass sod, water-stable aggregation in the soil was very markedly increased. Within a 65-year period, the greatest rate of improvement in aggregation occurred during the first 5 years in Kentucky bluegrass sod. Fertilization and manuring in a 4-year rotation containing 1 year of sod effected greater aggregation than that in the soil without such treatment.

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EFFECT OF ORGANIC ANIONS ON PHOSPHATE PRECIPITATION BY IRON AND ALUMINUM AS INFLUENCED BY pH[1]

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Active iron and aluminum, either in solution or as hydrated oxides, are considered to be the principal agents responsible for chemical fixation of phosphate in acid soils. Basic iron and aluminum phosphates are precipitated whenever soluble phosphate comes into contact with these agents. Maximum phosphate fixation is known to occur in very acid soils where iron and aluminum are most active; likewise the chemical precipitation of phosphate by solutions containing iron and aluminum shows the isoelectric point of the basic iron phosphate to be about pH 3 and that of basic aluminum phosphate to be about pH 4 (1, 2, 9, 16). In both systems, progressively less phosphate is precipitated as the pH is raised (3, 7, 17). Investigations by Swenson, Cole, and Sieling (16) showed that the presence of certain organic anions reduced greatly the amount of phosphate precipitated by iron at pH 3.0 and by aluminum at pH 4.0; however, these results do not necessarily indicate that such anions would have any marked effect in preventing phosphate precipitation at higher pH values.

The purpose of this investigation was to determine the influence of pH on the effectiveness of certain organic anions in preventing the precipitation of phosphate by iron and aluminum.

EXPERIMENTAL PROCEDURE

Establishment of standard values of phosphate precipitation by iron and aluminum at various pH levels

A standard procedure which was essentially the same as that previously reported by one of the authors (16) was used in this investigation. A solution of 1 millimol of $FeCl_3$ or $AlCl_3$ containing a known excess of HCl was mixed in a 250-ml. beaker with a solution containing 1 millimol of primary potassium acid phosphate. To this mixture were added enough NaCl to give a final concentration of 1 per cent and distilled water to establish a standard final volume of 125 ml. The resulting mixture was heated to boiling and sufficient 0.2 *N* NaOH (carbonate free) was added to adjust the equilibrium pH to the approximate value desired. The contents of the beaker were boiled continuously for ½ hour after addition of the NaOH to establish equilibrium. The mixture was cooled to room temperature for pH determination, reheated, and filtered while hot through Whatman No. 42 paper. The precipitate was washed three times successively by filling the filter paper with hot 1 per cent NaCl solution adjusted approximately to the pH of the system being studied. The precipitate containing the phosphate was dissolved in hot 1 per cent perchloric acid and the phosphate content was determined colorimetrically by an adaptation of the method of Sherman (12).

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[1] Contribution No. 736, Massachusetts Agricultural Experiment Station, Amherst. Part of a thesis submitted by the senior author to the graduate school of the University of Massachusetts in partial fulfillment of the requirements for the master of science degree.

Values were obtained for the percentage of phosphate precipitated by iron at progressive levels from pH 3 to pH 8, and by aluminum from pH 4 to pH 9. These values were used throughout the course of this investigation as standards for the amount of phosphate which could be precipitated by iron or aluminum at any given pH value.

Determination of influence of organic anions on precipitation of phosphate at various pH levels

The procedure used to determine the influence of organic anions on phosphate precipitation was essentially the same as that described for determining the effect of pH, with the exception that 1 millimol of the organic anion being studied was mixed with the phosphate solution before addition of the iron or aluminum solution and of the sodium hydroxide used to adjust the pH. This order of adding the reagents provided an equal opportunity for both the organic anion and the phosphate ion to compete for the iron or aluminum, thus expediting the establishment of equilibrium.

Values for the percentage of phosphate precipitated in the presence of each organic anion by iron at progressive levels from pH 3 to pH 8 and by aluminum from pH 4 to pH 9 were obtained by this method.

RESULTS

Many organic acids or their salts are produced in agricultural soils by the microbiological decomposition of plant and animal residues. Some of those found most extensively in soils were included in this investigation. Of these, citric, tartaric, and oxalic acids are known to form stable, soluble complexes with iron and aluminum. It is believed that the effectiveness of organic anions in preventing phosphate precipitation by iron and aluminum is dependent on the stability of the complexes formed. In selecting the other anions studied, consideration was given to chemical structure and composition; and series were established according to these considerations for the purpose of determining the types of compounds which could be expected to prove effective in preventing phosphate fixation. The characteristics given consideration were: (*a*) number of carboxyl groups; (*b*) presence of substituted amino groups; (*c*) presence and number of substituted hydroxyl groups; and (*d*) length of carbon chain.

The following acids were used to furnish the anions studied: *dl*-*α*-alanine, *dl*-aspartic, citric, *dl*-lactic, *dl*-malic, malonic, oxalic, succinic, and *dl*-tartaric. At any given pH level, the difference in the amount of phosphate precipitated by iron or aluminum in presence and in absence of each organic anion was assumed to be the measure of the effect that each anion exerted on the system. Values for the amount of phosphate precipitated in presence of organic anions are designated in the accompanying figures by the names of the respective anions; standard reference values of phosphate precipitation as influenced solely by pH are designated as "blank."

Series I: tartaric, malic, aspartic, and succinic acids

To determine the influence of substituted amino and hydroxyl groups on the effectiveness of otherwise similar organic anions in preventing phosphate precipitation by iron and aluminum, the following acids were used: tartaric (α,β-dihydroxy succinic), malic (hydroxy succinic), aspartic (amino succinic), and succinic. The results obtained are shown in figure 1 for the iron system and in figure 2 for the aluminum system.

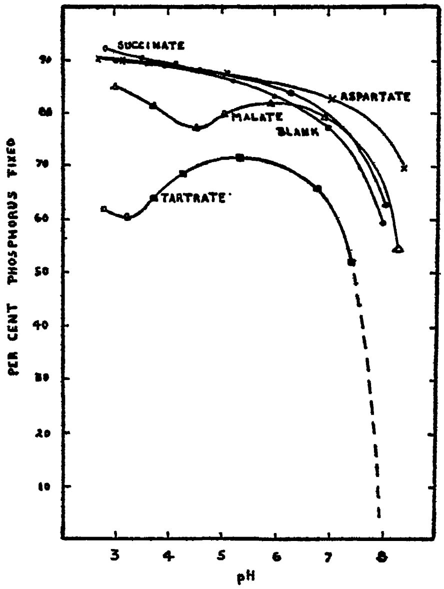

FIG. 1.

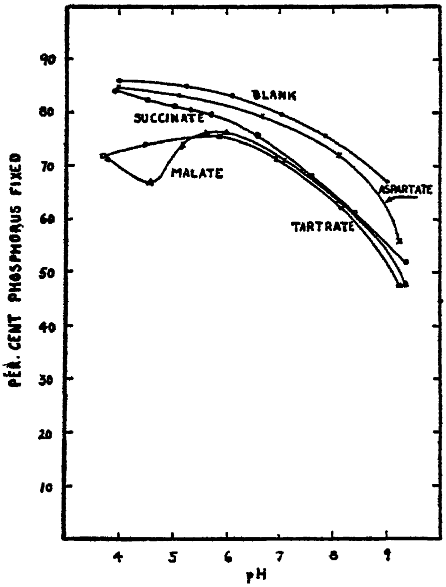

FIG. 2.

FIG. 1. INFLUENCE OF pH ON EFFECTIVENESS OF TARTRATE, MALATE, ASPARTATE, AND SUCCINATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY IRON

FIG. 2. INFLUENCE OF pH ON EFFECTIVENESS OF TARTRATE, MALATE, ASPARTATE, AND SUCCINATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY ALUMINUM

These findings show that the hydroxy-acid anions, tartrate and malate, were considerably more effective in preventing phosphate precipitation by both iron and aluminum than were succinate or aspartate ions, although the effectiveness of each varied at different pH values. The effect of the malate ion was greatest at a range between pH 4 and pH 5 for both elements; the tartrate ion had the greatest effect at the most acid pH level in each system.

In the iron system, tartrate prevented the precipitation of phosphate to a considerably greater degree throughout the entire pH range of 3 to 8 than did the other anions in this series. The malate ion was effective below pH 6, and succinate and aspartate ions did not decrease the amount of phosphate precipitated by iron at any pH value.

With aluminum, malate was superior to tartrate in reducing phosphate precipitation between pH 4 and 5.5, and was nearly equal to it above this pH range. Succinate ion became increasingly effective as the pH was raised, becoming nearly as effective as malate and tartrate above pH 6.5. Aspartate ion, on the other hand, caused only a slight uniform suppression of phosphate precipitation throughout the pH range 4 to 9.

Series II: oxalic, malonic, and succinic acids

The presence of hydroxyl groups was shown in the previous section to be an important factor in the ability of a dicarboxylic acid to prevent phosphate precipitation by iron or aluminum. It was considered desirable to investigate the influence of chain length on this property of organic anions by the use of a series of dicarboxylic acids having no functional groups. For this purpose the effects of oxalate, malonate, and succinate ions were compared; the results are shown in figures 3 and 4.

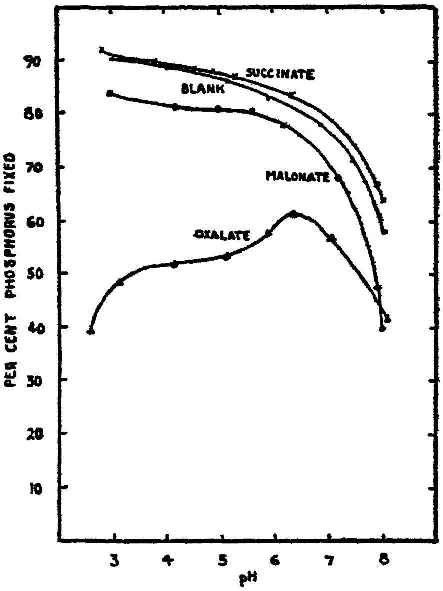

FIG. 3.

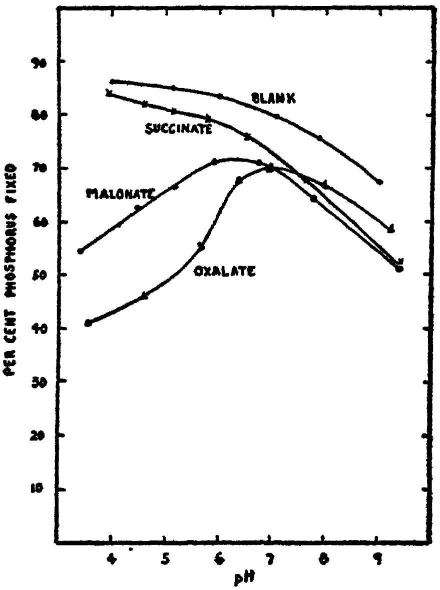

FIG. 4.

FIG. 3. INFLUENCE OF PH ON EFFECTIVENESS OF OXALATE, MALONATE, AND SUCCINATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY IRON

FIG. 4. INFLUENCE OF PH ON EFFECTIVENESS OF OXALATE, MALONATE, AND SUCCINATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY ALUMINUM

In very acid solutions the shorter-chain compounds had the greater relative effectiveness in reducing the amount of phosphate precipitated by both iron and aluminum; thus oxalate was most effective, followed in order by malonate and succinate. At the acid extreme, malonate was considerably more effective in preventing precipitation of phosphate by aluminum than by iron, indicating the formation of a more stable complex with aluminum at the low pH. Succinic acid, as shown in the previous series, had no capacity to prevent precipitation of phosphate by iron but increased in effectivness in that role at higher pH levels in the aluminum system.

Series III: lactic, malic, and citric acids and alanine

In previous series only dicarboxylic acids were considered. As monocarboxylic acids and tricarboxylic acids are also produced by microorganisms in the soil, they were included in this study. Lactic, malic, and citric acids are respectively mono-, di-, and tricarboxylic acids, and each has one hydroxyl group in its molecular structure. Figures 5 and 6 present the findings regarding the effectiveness of each in preventing phosphate precipitation by iron and aluminum.

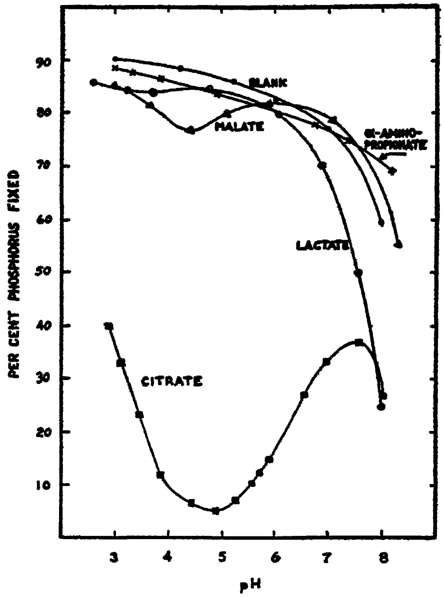

FIG. 5.

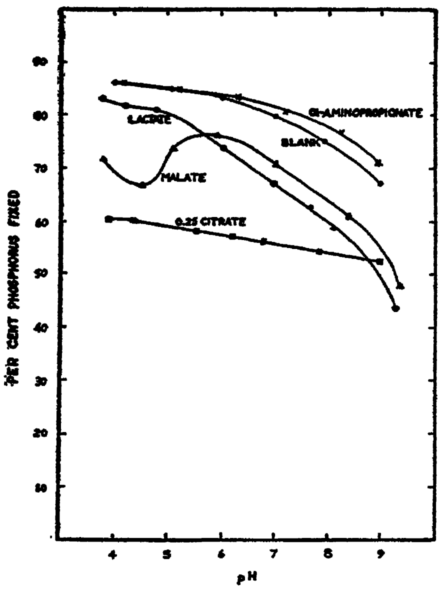

FIG. 6.

FIG. 5. INFLUENCE OF pH ON EFFECTIVENESS OF LACTATE, MALATE, CITRATE, AND α-AMINOPROPIONATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY IRON

FIG. 6. INFLUENCE OF pH ON EFFECTIVENESS OF LACTATE, MALATE, CITRATE, AND α-AMINOPROPIONATE IONS IN PREVENTING PHOSPHATE PRECIPITATION BY ALUMINUM

The tricarboxylic-acid anion, citrate, showed greater effectiveness than any other organic anion studied. In the iron system, its effect was greatest between pH 4 and pH 6, where 90 to 95 per cent of the phosphate remained in solution, whereas in absence of citrate, nearly 90 per cent was precipitated by the iron. In the aluminum system it was found that as little as 0.5 millimol of citrate completely prevented precipitation of basic aluminum phosphate when 1 millimol each of aluminum and phosphate were present. It was necessary, therefore, to reduce the amount of citrate to 0.25 millimol to get a measurable precipitation of basic aluminum phosphate which would show the influence of pH on this system.

Malate ion was superior to the lactate ion below pH 5.5, but above that value lactate proved to be more effective in preventing phosphate precipitation by both iron and aluminum; however, neither of these anions approached the effectiveness of citrate.

The relative influence of functional hydroxyl and amino groups is shown again in this series when a comparison between the effect of lactate (α-hydroxyproprionate) and alanine (α-aminoproprionate) is made. Lactate is effective in inhibiting precipitation of phosphate by aluminum throughout the pH range of 4 to 9 and the effect gradually increases as the pH increases; however, alanine has no appreciable effect. With iron, lactate was effective in preventing phosphate precipitation at pH values above 5.5, whereas alanine showed a slight but not significant effect from pH 3.0 to pH 7.0.

DISCUSSION

The importance of organic matter in maintaining soil productivity has long been recognized. Its functions in this respect, however, are usually described in general terms such as: increases aggregation of soils; increases water-holding capacity; increases base-exchange capacity. On the other hand, its role in the nitrogen cycle in soils has been studied extensively, and the fundamental biochemical reactions involving nitrogen and organic matter are well established. Organic matter controls nitrogen in soils, and *vice versa* (15). The functions of organic matter in controlling the availability of other plant nutrient elements are not so well defined.

That organic matter has a beneficial action in keeping phosphate available for plant use has been reported by Hester and Shelton (4), Midgley and Dunklee (6), Pierre (8), and others (5, 11). This beneficial effect has been attributed to: (*a*) the protective action of organic colloids or gross organic matter in preventing soluble phosphates from coming into contact with the active iron and aluminum; (*b*) the action of carbon dioxide, produced by organic matter decomposition, in dissolving certain phosphatic materials or in tying up the active iron; (*c*) formation of organic phosphates, which are less firmly fixed by soils than are inorganic phosphates; and (*d*) mineralization by bacteria of organic matter containing phosphates with the resultant release of phosphate for plant use.

Swenson, Cole, and Sieling (16) assigned a specific role to organic matter in making phosphate more readily available. They observed that certain organic anions were effective in preventing phosphate precipitation by iron and aluminum and in liberating fixed phosphate from the basic phosphates of these elements at very low pH values. The most effective organic anions were those which were known to form stable complexes with iron and aluminum, and these workers suggested that the active anions were produced by microorganisms during decomposition of organic matter in soils.

The research reported here substantiates the findings of Swenson *et al.* and goes further to show that several organic anions are effective in preventing precipitation of phosphate by iron and aluminum at pH values common to agricultural soils. Some are most effective at low pH values; some at the moderately acid range of pH 5 to pH 6; and others at the neutral point or above. Each anion changes in effectiveness as the pH changes. Apparently the stability of the complex formed between each anion and the iron or aluminum is influenced by pH. Therefore, the pH of greatest stability of the complex coincides with the greatest effectiveness of the anion in preventing phosphate fixation. The most obvious example of this is shown by the effect of citrate on precipitation of phosphate by iron. The ability of the citrate to form a complex with the iron increases progressively with an increase in pH from 3.0 to 4.8 and then gradually decreases as the pH is raised to 7.5.

The most significant information found in this research is that at any pH within the entire range of values for agricultural soils there are some organic anions that are markedly effective in preventing precipitation of phosphate by iron or aluminum. The most effective anions found in this study were citrate, oxalate, tartrate, malate, and malonate, and it is important to note that these are the very ones which investigators (13, 19) have found to be produced in greatest quantity by the action of microorganisms on organic matter in soils. It seems obvious that many other organic anions produced in the soil would be equally effective. Uronic acids and the polyuronides occur in soils in considerable quantities—as much as 30 per cent of the organic matter in some instances (14, 18). Preliminary investigation of these important soil substances has indicated that they are very effective in preventing phosphate fixation. A more detailed study of the influence of uronides on phosphate fixation and on soil-forming processes is being made.

The old adage, "Lime and lime without manure make both farm and farmer poor," finds justification in the results obtained in this study. The influence of an increase in pH of either the iron or the aluminum system which contains phosphate but no organic anion can be considered analogous to raising the pH of a purely inorganic soil by "liming without manure." In this case an increase in pH from 4 to 6 resulted in freeing only 7 per cent of the phosphate which had been fixed by the iron at the lower pH value. A comparable increase in pH caused the release of less than 4 per cent of the phosphate from basic aluminum phosphate.

On the other hand, application of manure to soils results in the microbiological production of organic anions and the creation of conditions very similar to the chemical systems containing organic anions which were studied here. The release of phosphate by organic anions greatly exceeds that caused by raising the pH. For example, at pH 4.0, malate, tartrate, oxalate, and citrate respectively released 11, 25, 43, and 89 per cent of the phosphate from basic iron phosphate and 18, 15, 50, and 100 per cent of the phosphate from the basic aluminum phosphate. The amounts of phosphate released throughout the entire pH range common to agricultural soils are of similar magnitudes even though the order of effectiveness of the different anions may change. The authors believe that the increases in phosphate availability which several investigators (7, 8, 10) have reported as resulting from the liming of acid soils were due primarily to presence of greater quantities of organic anions produced as a result of stimulated microbiological activity. Thus presence of an adequate supply of easily decomposable organic matter would be a prerequisite for obtaining the most favorable response to the liming of acid soils.

The organic anions produced in the soil are nature's effective agents for preventing phosphate fixation by iron and aluminum in neutral and acid soils and for making available that phosphate which has already been fixed. Practical agriculturalists should be able to get greater efficiency from natural and applied phosphates by management practices which encourage production of these effective agents in the soil.

SUMMARY AND CONCLUSIONS

Nine organic acids, some of which are found extensively in soils, were investigated to determine their effectiveness in preventing phosphate precipitation by iron and aluminum at various pH values. The nine acids used were: *dl*-α-alanine, *dl*-aspartic, citric, *dl*-lactic, *dl*-malic, malonic, oxalic, succinic, and *dl*-tartaric.

Each acid differed from the others in its effectiveness in preventing phosphate precipitation by iron and aluminum at different pH values. In addition, the specific effect of each acid with iron was different from that with aluminum although there was a general similarity of effect in some cases. Some of the acids were most active at low pH levels, some in moderately acid solutions, and others at the neutral point or above.

The most effective acids were citric, oxalic, tartaric, malonic, malic, and lactic and their greatest effectiveness was in the more acid pH range, although some were active also at higher pH values. These organic acids occur in soils in considerable quantity as a result of the action of microorganisms on organic matter. They are therefore operative in forming stable complexes with iron and aluminum in a pH range where these elements are most active in phosphate fixation, thus helping to prevent fixation.

Citrate was the most active anion in preventing phosphate precipitation with both iron and aluminum. One millimol completely complexed 1 millimol of aluminum, and no phosphate was precipitated in the pH range 4 to 9. With iron, citrate was most effective between pH 4.0 and pH 6.0 where 1 millimol released more than 90 per cent of the phosphate from 1 millimol of basic iron phosphate.

The structure of the organic anion was of importance in determining its efficiency in preventing phosphate precipitation by iron or aluminum. The general observations concerning the effect of structure are as follows:

Amino group. As shown by alanine and aspartic acid, the functional amino group has no significant effect on the ability of the organic anion to suppress phosphate precipitation.

Hydroxyl group. The effectiveness of the organic anion is increased progressively as the number of functional hydroxyl groups is increased in an otherwise unchanged molecule. Tartrate (α, β, dihydroxysuccinate) has the greatest ability, malate (α-hydroxysuccinate) has somewhat less ability, and succinate has the least.

Number of carboxyl groups. As the number of carboxyl groups is increased, the effectiveness of the organic anion is increased, as shown by the series: lactate, malate, and citrate.

Length of carbon chain. A short chain-length increases the effectiveness of the anion, as shown by results for the saturated unsubstituted acids oxalic, malonic and succinic.

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USE OF ACID, ROSE BENGAL, AND STREPTOMYCIN IN THE PLATE METHOD FOR ESTIMATING SOIL FUNGI[1]

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Soon after the agar plate method for studying bacteria was developed it was adapted for use in determining numbers and kinds of soil fungi. Inasmuch as bacteria and actinomycetes are relatively more numerous than fungi in most soils, it was necessary to add to the medium some material which would prevent the growth of these forms and still allow the fungi to grow. The best method developed, and one that has become standard procedure, is incorporation of a naturally acid material into the agar, or artificial acidification of the medium with an acid such as sulfuric, citric, or lactic. The artificial media most commonly used in the plate method for soil-fungus studies contain a relatively high concentration of carbohydrate, such as dextrose, and a suitable nitrogen source, such as peptone or nitrate (2, 4, 7).

The plate method as at present constituted has resulted in many important contributions to our knowledge of the nature and activities of soil fungi. Nevertheless, this method has several important disadvantages, some of which are as follows: 1. Not all soil fungi will grow on any one medium. The nutritional requirements of different groups are so diverse that it is difficult to perfect a medium which will allow growth of all types, and one can only hope to prepare a medium on which the greatest possible numbers and kinds will develop. 2. Several common soil fungi will not grow on a medium that is sufficiently acid to prevent growth of all bacteria and actinomycetes. 3. The faster-growing fungi, or "spreaders," may cover all or most of the plate before the slower-growing types become established. One may thus get a false picture of the fungus population.

Recently, various attempts have been made to improve the plate method for studying fungi. Tyner (5) asserted that boric acid prevented growth of bacteria and gave higher counts of fungi than sulfuric acid. The work of Smith and Dawson (4), and unpublished data by the present writer, have been completely at variance with this. With boric acid, many soils yielded almost sterile plates; others were covered with numerous bacterial colonies; and all contained relatively few fungus colonies. Smith and Dawson suggested use of rose bengal in fungus media for preventing bacterial growth. This dye in a concentration of 1 part in 15,000 eliminated all actinomycetes and most bacteria and reduced spreading of mold colonies. The comparatively few bacteria that did develop on the plates could be easily distinguished from the fungus colonies. Counts of fungi were higher in the media containing rose bengal (pH 6.8) than in the acidified media (pH 4.2). Fewer bacteria developed on glucose–nitrate–soil-extract agar than on peptone-dextrose agar, but fungus counts were similar.

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[1] Paper No. 617, University of California Citrus Experiment Station, Riverside, California.

Dawson and Dawson (1) in a later study plated pure cultures of 12 common fungi, using glucose–nitrate–soil-extract agar with and without 1:15,000 rose bengal. The only evidence of fungistatic activity of the dye was a reduction in size of the colonies.

Littman (3) developed a peptone–dextrose–oxgall–crystal-violet–streptomycin agar for primary isolation of pathogenic fungi from material containing a mixed flora. He observed that growth of both gram-positive and gram-negative bacteria was inhibited on this medium, and that discrete, nonspreading fungus colonies developed. It was suggested that this medium might be successfully used for fungus studies in other fields. Littman's medium was applied to soils by Wilson and Fults[2] in a study of the effect of 2,4-dichlorophenoxyacetic acid on the kinds of fungi in a clay loam soil.

Much plating to determine the numbers and kinds of soil fungi has been done in this laboratory. For this reason, a study was made to determine the effectiveness, in suggested and new combinations, of some of the materials recently proposed for preventing growth of bacteria and actinomycetes and spreading of fungus colonies on various mold media, and to compare the numbers and kinds of fungi developing on the plates with those obtained by our usual method, namely, peptone-dextrose agar acidified to pH 4.0 with surfuric acid.

METHODS

Soil samples were collected from virgin and cultivated areas with a 1-inch sample tube. For each location, 20 holes were made. Most soils were sampled at depths of 0 to 12 and 12 to 24 inches. The soil from both depths and from each of five holes was combined, mixed, and subsampled. A few soils were sampled at depths of 0 to 6, 6 to 18, 18 to 36, and 36 to 48 inches. For these, all 20 samples from each depth were combined, mixed, and subsampled. The subsamples were plated the day they were taken, or were placed in the refrigerator and plated the following morning.

For preliminary studies three basal media were employed; namely, peptone-dextrose agar (6), peptone-dextrose-oxgall agar (3), and glucose–nitrate–soil-extract agar (4):

Peptone dextrose agar. Tap water, 1,000 ml.; dextrose, 10 gm; peptone, 5 gm.; KH_2PO_4, 1 gm.; $MgSO_4 \cdot 7H_2O$, 0.5 gm.; agar, 20 gm.

Peptone-dextrose-oxgall agar. Distilled water, 1,000 ml.; dextrose, 10 gm.; peptone, 10 gm.; oxgall, 15 gm.; agar, 20 gm.

Glucose–nitrate–soil-extract agar. Glucose, 10 gm.; $NaNO_3$, 1 gm.; K_2HPO_4, 1 gm.; agar, 18 gm.; soil extract, 1,000 ml. (prepared by autoclaving 500 gm. soil in 1,200 ml. water for 1 hour and filtering).

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[2] Wilson, V. E., and Fults, J. L. Qualitative effects of the sodium salt of 2,4-dichlorophenoxyacetic acid on the fungi isolated from a clay loam soil. [Mimeographed abstract of paper presented at 1948 meetings of the Soil Science Society of America, Fort Collins, Colorado.] 1948.

To prevent growth of bacteria and actinomycetes on the plates, the following materials were used: sulfuric acid (pH 4); rose bengal, 1 part in 15,000 of medium; and streptomycin (streptomycin sulfate equivalent to 15 and 30 γ per milliliter of medium); streptomycin plus crystal violet, 1 part in 100,000; and streptomycin plus rose bengal, 1:15,000 and 1:30,000. Rose bengal and crystal violet were added to the media with the original ingredients. Sulfuric acid and streptomycin were added after the media had been melted and cooled sufficiently to pour the plates.

Plates were poured from appropriate dilutions in replicas of eight for samples from depths of 0 to 6, 0 to 12, or 6 to 18 inches, and in replicas of four for samples from depths of 12 to 24, 18 to 36, or 36 to 48 inches. After incubation of the plates for 1 week at approximately 25° C., the fungus and bacterial colonies were counted. The fungus colonies were examined macroscopically and microscopically for identification. Those that could not be identified were allowed to develop further or were picked, plated, and streaked on various fungus media and examined. Forms that could not be identified after this procedure were numbered. Dark-colored forms were numbered D1, D2, etc.; and hyalin cultures, M1, M2, etc.

RESULTS

Preliminary studies gave variable results. Streptomycin alone allowed the growth of relatively large numbers of bacteria and did not reduce spreading. In combination with rose bengal or with crystal violet, spreading was markedly reduced, and the plates were virtually free of bacterial colonies. Rose bengal alone was effective in reducing spreading of many fungus colonies and in eliminating most bacterial growth on plates from some soils, whereas on others relatively large numbers of bacterial colonies developed. Acid was the best means of checking growth of bacteria, but, as is well known, it does not reduce spreading of many rapidly growing fungi. The crystal-violet–streptomycin combination gave best results in the rich peptone-dextrose-oxgall medium. As the two dyes made identification of some fungus types more difficult, it was necessary to make more transfers to other media when these materials were used. The crystal violet was more disadvantageous from this point of view. Use of 1:15,000 or 1:30,000 rose bengal in place of the crystal violet in the oxgall medium was an improvement. Bacterial colonies were larger and spreading of some fungus colonies was greater on the glucose–nitrate–soil-extract agar than on the other media. Rose bengal completely inhibited growth of actinomycetes.

As a result of the preliminary studies, acidified peptone-dextrose agar and both peptone-dextrose agar and glucose–nitrate–soil-extract agar with 1:15,000 rose bengal and with 1:30,000 rose bengal plus 30 γ per milliliter of streptomycin, were selected for more detailed studies. Littman's oxgall medium with streptomycin and rose bengal or crystal violet was an excellent medium, but since it had no particular advantage over the peptone-dextrose agar it was not included.

The effect of these media on the number and kind of fungi and number of bacteria capable of developing on each, in several soils, is recorded in tables 1 to 4, and in figure 1. Only representative results are presented in the tables.

Virgin Ramona sandy loam contained very few bacteria capable of growing in the presence of either rose bengal or rose bengal plus streptomycin. The highest

TABLE 1

Effect of various media and bacterial growth preventives on number and kind of fungi in virgin Ramona sandy loam

FUNGUS	SOIL FROM 0–12-INCH DEPTH					SOIL FROM 24–48-INCH DEPTH				
	Peptone-dextrose agar			Glucose-nitrate-soil-extract agar		Peptone-dextrose agar			Glucose-nitrate-soil-extract agar	
	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
	Approximate number of bacteria (per gram dry soil) capable of growing on medium									
	0	7,000	4,000	20,000	2,000	0	1,000	0	8,000	0
	Approximate number of fungi per gram dry soil									
	50,000	92,000	98,000	85,000	95,000	7,000	9,000	13,000	11,000	11,000
	Approximate percentage concentration of fungi on plates									
Aspergillus sydowi	16	10	9	9	12	0	0	1	2	0
Cladosporium herbarum	<1	2	<1	0	0	0	0	0	0	0
Fusarium spp.	3	2	1	<1	3	3	2	<1	1	2
Mucor spp.	2	0	<1	<1	1	<1	3	5	4	9
Penicillia, blue-green	<1	<1	2	2	1	<1	2	6	1	6
Penicillium humicola	0	0	0	0	0	2	6	4	10	2
P. lilacinum	2	8	8	8	8	38	38	19	30	30
P. nigricans	46	23	17	20	23	28	18	12	12	26
P. restrictum	14	12	17	10	13	9	11	8	5	8
Stysanus stemonites	0	12	13	17	10	0	2	2	2	1
Trichoderma spp.	4	5	3	3	2	0	0	0	0	0
Fungus D30	<1	14	20	17	16	2	10	21	19	8
Other species*	12	11	9	13	11	17	8	21	14	8
	Total number of identified species of fungi									
	15	17	18	17	20	8	10	12	13	11

* Including unidentified fungus colonies.

count (20,000) would be equivalent to an average of 20 colonies on a 1:1,000 dilution plate, or 4 colonies on a 1:5,000 dilution plate. The fungus counts in the soil samples from depths of 0 to 12 and 12 to 24 inches, respectively, were ap-

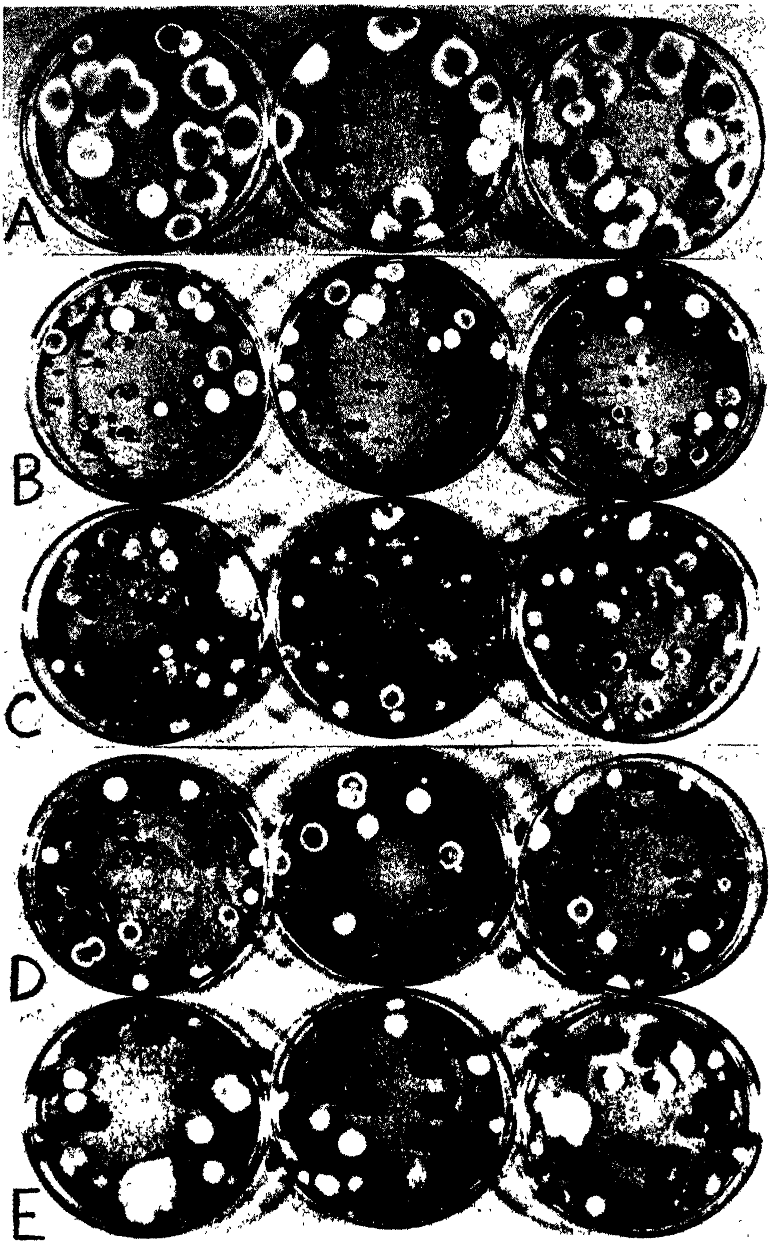

FIG. 1. COMPARATIVE EFFECTIVENESS OF SULFURIC ACID, ROSE BENGAL, AND STREPTOMYCIN IN PREVENTING BACTERIAL GROWTH ON FUNGUS PLATES FROM HANFORD SANDY LOAM

A, peptone-dextrose agar adjusted to pH 4 with H_2SO_4; B, peptone-dextrose agar plus 1:15,000 rose bengal; C, glucose–nitrate–soil-extract agar plus 1:15,000 rose bengal; D, peptone-dextrose agar plus 1:30,000 rose bengal plus streptomycin (30 γ/ml.); E, glucose–nitrate–soil-extract agar plus 1:30,000 rose bengal plus streptomycin (30 γ/ml.). All plates from same soil dilution. Note small bacterial colonies on B plates, large bacterial colonies on C plates, and comparative absence of bacterial colonies on D and E plates.

proximately 80 and 55 per cent higher in both the rose bengal and rose bengal plus streptomycin plates than in those containing acidified agar. This difference, to a considerable degree, resulted from the relatively large numbers of *Stysanus stemonites* and Fungus D30 colonies on the former media, and their absence, or virtual absence, on the acid medium.

Cultivated Ramona sandy loam (table 2) contained comparatively large numbers of bacteria which were not depressed by the rose bengal. The number of bacterial colonies developing on the media was apparently sufficient to reduce the number of fungus colonies. Plates with acid or with rose bengal plus streptomycin in the medium contained very few bacterial colonies. Total fungus counts were a little lower on the acid medium. Two fungi, D14 and D30, did not occur on the acid medium but developed on the others.

The numbers and kinds of fungi developing from cultivated Hanford sandy loam (table 3) were similar on all the media. Comparatively large numbers of bacterial colonies were found on the media containing rose bengal alone.

Additional soil platings gave results similar to those above. Some soils contained very few bacteria capable of growing in the presence of 1:15,000 rose bengal, whereas others contained relatively large numbers. Growth of bacteria was sufficient to reduce numbers and kinds of fungi from some soils but not from others. In all platings, the media containing rose bengal and streptomycin allowed growth of relatively few or no bacteria. In general, there was no consistent difference in the number of bacterial colonies developing on the glucose–nitrate–soil-extract agar and on the peptone-dextrose agar, but there were more large, slimy colonies on the glucose–nitrate–soil-extract agar (fig. 1). Although rose bengal reduced the size of most fungus colonies, several forms tended to spread on the glucose–nitrate–soil-extract agar containing this dye.

Several more soils were plated on peptone-dextrose agar containing either acid or rose bengal and streptomycin. Table 4 records the results for cultivated Hanford sandy loam and cultivated Placentia sandy loam. Total fungus counts in soil from the surface 6 inches were approximately 80 to 90 per cent higher in the medium containing rose bengal and streptomycin. The difference in numbers tended to decrease at lower soil depths but the counts remained higher than in the medium containing sulfuric acid. *Fusarium* sp. 6, *Stysanus stemonites*, Fungus D14, and Fungus M4 developed in relatively high concentration on some of the plates containing the rose-bengal–streptomycin agar, but failed to grow on the acid agar.

To test the effects of the various bacterial growth inhibitors used in this study on apparent growth of fungi, 117 cultures recently isolated from the soil on one or more media were streaked on peptone-dextrose agar and on glucose–nitrate–soil-extract agar containing the inhibitors. The results of this study are reported in table 5. Sulfuric acid (pH 4) in peptone-dextrose agar entirely or virtually prevented growth of 11 fungi, greatly reduced growth of 8, and slightly to moderately depressed development of 37. In the same medium, 1:15,000 rose bengal almost prevented growth of 3 cultures, markedly retarded development of 12, and slightly to moderately reduced growth of 90. One part in 30,000 rose bengal

TABLE 2

Effect of various media and bacterial growth preventives on number and kind of fungi in cultivated Ramona sandy loam

FUNGUS	SOIL FROM 0–12 INCH DEPTH					SOIL FROM 12–24 INCH DEPTH				
	Peptone-dextrose agar			Glucose-nitrate-soil-extract agar		Peptone-dextrose agar			Glucose-nitrate-soil-extract agar	
	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
	Approximate number of bacteria (per gram dry soil) capable of growing on medium									
	7,000	425,000	7,000	375,000	37,000	0	204,000	3,000	202,000	5,000
	Approximate number of fungi per gram dry soil									
	75,000	63,000	88,000	70,000	108,000	18,000	14,000	19,000	11,000	19,000
	Approximate percentage concentration of fungi on plates									
Acrostalagmus spp.	<1	<1	4	2	3	0	0	2	0	0
Aspergillus versicolor	10	8	6	14	10	<1	2	0	0	0
Fusarium solani	20	17	12	27	19	34	50	30	64	44
Fusarium spp.	7	8	4	2	6	3	2	<1	0	0
Gliocladium penicilloides	<1	3	8	8	5	0	0	0	0	2
Monotospora brevis	<1	3	4	2	2	0	0	0	0	2
Mucor spp.	2	4	2	5	1	5	1	5	6	6
Oospora variabilis	5	2	3	5	0	0	0	0	0	0
Penicillia, blue-green	9	10	11	7	3	0	1	<1	0	0
Penicillium nigricans	2	4	4	2	2	1	1	1	2	<1
Pyrenochaeta sp.	14	11	10	10	12	27	30	17	14	19
Spicaria sp.	2	2	0	2	1	1	0	0	0	0
Trichoderma lignorum	2	<1	1	<1	<1	<1	3	<1	0	0
Fungus D1	12	7	5	0	7	18	4	36	9	23
Fungus D14	0	1	4	2	6	<1	2	1	0	1
Fungus D30	0	1	8	<1	6	0	0	2	0	0
Fungus M2	2	1	1	1	0	0	0	1	0	0
Other species*	12	17	13	11	17	10	4	5	5	3
	Total number of identified species of fungi									
	23	22	28	22	22	13	12	13	5	9

* Including unidentified fungus colonies.

TABLE 3

Effect of various media and bacterial growth preventives on number and kind of fungi in cultivated Hanford sandy loam

FUNGUS	SOIL FROM 2–12-INCH DEPTH					SOIL FROM 12–24-INCH DEPTH				
	Peptone-dextrose agar			Glucose-nitrate-soil-extract agar		Peptone-dextrose agar			Glucose-nitrate-soil-extract agar	
	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
	Approximate number of bacteria (per gram dry soil) capable of growing on medium									
	0	205,000	0	330,000	6,000	0	137,000	1,000	190,000	0
	Approximate number of fungi per gram dry soil									
	53,000	43,000	58,000	50,000	60,000	30,000	26,000	29,000	25,000	31,000
	Approximate percentage concentration of fungi on plates									
Acrostalagmus cinnabarinus	0	<1	2	1	<1	0	0	<1	0	0
Aspergillus versicolor	1	1	4	0	1	<1	<1	0	0	<1
Fusarium oxysporum	<1	<1	3	1	1	0	0	0	0	0
F. solani	13	5	7	13	6	9	8	8	4	10
Hormodendrum olivaceum	7	1	6	4	8	0	0	0	0	0
Monotospora brevis	0	2	<1	1	2	<1	0	<1	1	2
Mucor spp	5	4	2	4	6	<1	0	1	<1	1
Penicillia, blue-green	2	1	5	2	5	0	0	0	0	0
Penicillium nigricans	24	33	33	22	35	25	23	25	30	23
P. vinaceum	7	6	6	1	6	3	5	1	4	1
Pyrenochaeta sp	22	22	20	36	17	37	48	40	45	49
Trichoderma lignorum	1	3	<1	0	<1	0	0	<1	0	1
Fungus D1	14	15	8	5	9	23	12	20	10	11
Fungus D14	0	0	2	1	1	0	0	1	0	0
Other species*	4	6	2	9	3	2	4	3	6	2
	Total number of identified species of fungi									
	13	13	18	15	16	10	6	12	7	11

* Including unidentified fungus colonies.

TABLE 4

*Effect of sulfuric acid and of rose bengal plus streptomycin as bacterial growth preventives on number and kind of fungi in two soils**

FUNGUS	HANFORD SANDY LOAM								PLACENTIA SANDY LOAM							
	0–6 inches		6–18 inches		18–36 inches		36–48 inches		0–6 inches		6–18 in ches		18–36 inches		36–48 inches	
	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.	H_2SO_4	R. B. + Strep.
	Approximate number of fungi in thousands per gram dry soil															
	210	380	75	115	9	14	8	9	240	460	60	100	7	12	11	12
	Approximate percentage concentration of fungi on plates															
Aspergillus candidus	1	0	0	0	0	0	0	0	7	2	2	0	0	2	2	2
A. nidulans	<1	0	0	0	0	0	0	0	2	4	0	0	0	6	0	0
A. niger	<1	<1	<1	1	0	0	0	0	9	5	2	1	0	2	0	0
A. sydowi	10	14	1	8	0	0	<1	3	8	4	11	1	4	<1	5	11
A. versicolor	10	8	7	6	0	2	0	0	28	19	19	15	9	13	13	14
Fusarium solani	16	11	22	20	69	33	48	36	14	11	27	21	36	17	29	23
F. sp. 6	0	15	0	11	0	0	0	0	0	0	0	0	0	0	0	0
Hormodendrum spp.	9	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Monotospora brevis	<1	1	0	<1	<1	2	0	0	0	2	<1	<1	0	0	2	<1
Mucor spp.	<1	2	<1	2	0	0	0	0	0	2	0	1	0	0	5	3
Penicillia, blue-green	5	8	2	1	0	1	3	0	2	4	8	5	8	11	8	3
Penicillium lilacinum	<1	<1	14	2	3	3	0	2	3	6	10	2	4	0	4	0
P. restrictum	<1	<1	2	1	0	0	3	3	0	0	2	0	4	0	0	0
Pyrenochaeta sp.	2	5	19	8	6	8	0	11	0	0	6	7	22	9	14	14
Stysanus stemonites	0	20	0	8	0	21	0	18	0	11	0	12	0	14	0	6
Trichoderma lignorum	0	<1	0	0	0	0	0	0	3	2	<1	1	8	2	2	0
Fungus D1	0	2	14	4	12	19	38	6	0	0	<1	3	0	2	0	3
Fungus D14	0	0	0	2	0	0	0	0	0	8	0	3	0	7	0	2
Fungus D30	0	<1	2	5	0	5	0	2	0	3	0	2	0	0	0	0
Fungus M4	0	0	0	4	0	0	0	0	0	11	0	10	0	0	0	2
Other species	45	9	17	17	10	6	8	19	24	6	12	15	5	15	16	17
	Total number of identified species															
	26	27	16	23	7	11	5	9	17	22	19	22	8	14	12	16

* Peptone dextrose agar adjusted to pH 4 with H_2SO_4, or used with rose bengal, 1:30,000, plus streptomycin, 30 γ/ml.

TABLE 5

*Effect of various bacterial growth preventives on development of streak-plate cultures of soil fungi**

FUNGUS	PEPTONE-DEXTROSE AGAR					GLUCOSE-NITRATE-SOIL-EXTRACT AGAR		
	Plain	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Streptomycin (30γ/ml.)	Plain	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
Acrostalagmus albus	++++	+++	+++	+++	++++	++++	+++	+++
A. cinnabarinus	++++	+	+++	+++	++++	++++	+++	+++
A. sp. 1	++++	++	+++	++++	++++	++++	++++	++++
Acrothecium robustum	++++	++	+	++	++++	++++	+++	+++
Alternaria tenuis	++++	+++	++	+++	++++	++++	+++	+++
Aspergillus candidus	++++	++++	++++	++++	++++	++++	+++	+++
A. clavatus	++++	+++	++	+++	++++	++++	++	+++
A. nidulans	++++	++++	+++	+++	++++	++++	++++	++++
A. niger	++++	++++	+++	+++	++++	+++	++	++
A. ochraceus, strain 1	++++	++++	+++	+++	++++	++++	+++	+++
A. ochraceus, strain 2	++++	+++	++	+++	++++	+++	++	++
A. sulfureus	++++	++++	++	++++	++++	+++	+++	+++
A. sydowi	++++	+++	++++	++++	++++	++++	++++	++++
A. versicolor	++++	++++	++++	++++	++++	++++	++++	++++
A. sp. 1	++++	++++	+++	++++	++++	+++	++	++
Botrytis sp.	++++	++++	++	++	++++	+++	++	++
Cephalosporium curtipes	++++	++++	+++	++++	++++	++++	+++	++++
Chaetomium sp.	+++	0	+	+++	+++	++++	++++	++++
Circinella sydowi	+++	+	++	++	+++	++++	++++	++++
Cladosporium herbarum	++++	++++	+++	++++	++++	+++	++	++
Coremium sp.	++++	++++	+++	+++	++++	++++	+++	+++
Cinninghamella bertholletiae	++++	++++	+++	++++	++++	++++	++++	++++
C. echinulata	++++	++++	+++	++++	++++	++++	+++	++++
C. sp. 1	++++	++++	+++	+++	++++	++++	+++	+++
Cylindrocarpon radicicola	++++	++++	+++	+++	++++	++++	+++	+++
Epicoccum purpuracens	++++	++++	+++	+++	++++	++++	+++	+++
Fusarium oxysporum	++++	+++	+++	+++	++++	+++	+++	+++
F. solani	++++	+++	+++	+++	++++	++++	+++	+++
F. sp. 3	++++	+++	++	+++	++++	++++	+++	+++
F. sp. 4	++++	++++	++	+++	++++	++++	+++	+++
F. sp. 5	++++	++++	+++	+++	++++	++++	+++	+++

TABLE 5—*Continued*

FUNGUS	PEPTONE-DEXTROSE AGAR					GLUCOSE-NITRATE-SOIL-EXTRACT AGAR		
	Plain	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Streptomycin (30γ/ml.)	Plain	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
F. sp. 6	++++	+	+++	+++	++++	++++	++++	++++
F. sp. 7	++++	+++	+++	+++	++++	+++	++	++
F. sp. 8	++++	+++	++	+++	++++	++++	+++	+++
F. sp. 9	+++	0	++	++	+++	++++	++++	++++
Gliocladium penicilloides	++++	++++	+++	++++	++++	+++	+++	+++
G. sp. 1	++++	+++	++	+++	++++	++++	++	+++
Hormodendrum cladosporioides	++++	++++	++++	++++	++++	++++	++++	++++
H. hordei	++++	++++	++++	++++	++++	++++	++++	++++
H. olivaceum	++++	++++	++++	++++	++++	++++	++++	++++
H. pallidum	++++	++++	+	+++	++++	++++	+++	+++
H. sp. 1	++++	+++	+++	+++	++++	++++	+++	+++
H. sp. 2	++++	++++	++++	++++	++++	++++	++++	++++
Monilia pruinosa	++++	+++	+++	+++	++++	+	Trace	Trace
Monotospora brevis	+++	++	+	+++	++	++++	++++	++++
Mucor sp.	++++	++++	+++	+++	++++	++++	+++	+++
Nematagonium sp.	++++	++++	++	++	++++	++++	+++	+++
Oospora variabilis	++++	++++	+	+	++++	+	Trace	+
Penicillium geophilum	++++	++++	+++	+++	++++	++++	+++	+++
P. humicola	++++	++++	++++	++++	++++	+++	+++	+++
P. lilacinum	++++	++++	+++	+++	++++	++++	+++	+++
P. nigricans	++++	++++	+++	+++	++++	++++	+++	+++
P. restrictum	++++	++++	+++	+++	++++	++++	+++	+++
P. variabile	++++	++++	++	++	++++	+++	++	++
P. vinaceum	++++	++++	+++	+++	++++	++++	+++	+++
P. sp. 3	++++	++++	++	++++	++++	++	++	++
P. sp. 4	++++	++++	+++	+++	++++	+++	++	++
Phoma sp.	++++	+	+	+++	++++	++++	+++	+++
Pyrenochaeta decipiens	++++	+++	++	++	++++	++++	+++	+++
P. sp. 1	++++	++++	+++	+++	++++	++++	+++	+++
Rhizopus nigricans	++++	+++	++	++	++++	++	+	+
Sclerotium sp.	++++	++++	++	++	++++	++++	+++	+++
Spicaria divaricata	++++	++++	+++	+++	++++	+	Trace	Trace
S. sp. 1	++++	++++	++++	++++	++++	++	++	++
Stemphylium consortiale	++++	++	++	+++	++++	++++	+++	+++
S. piriforme	++++	++	+++	+++	++++	++++	+++	+++
S. sp. 1	++++	++++	++	+++	++++	++++	+++	+++
Stysanus stemonites	++++	Trace	+++	++++	++++	++++	++++	++++
Syncephalastrum racemosum	++++	+++	+++	+++	++++	+++	+++	+++

TABLE 5—*Continued*

FUNGUS	PEPTONE-DEXTROSE AGAR					GLUCOSE-NITRATE-SOIL-EXTRACT AGAR		
	Plain	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Streptomycin (30γ/ml.)	Plain	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.
Thieleviopsis basicola	++++	++++	++	++	++++	++	+	+
Torula sp. 1	++++	++++	+++	+++	++++	++++	+++	+++
T. sp. 2	++++	++++	++	+++	++++	++++	+++	+++
Trichoderma koningi	++++	++++	++	++	++++	++++	++	+++
T. lignorum	++++	++++	++	++	++++	++++	+++	+++
Volutella sp. 1	++++	++++	+++	+++	++++	++++	+++	+++
V. sp. 2	++++	++	++++	++++	++++	+++	+++	+++
Fungus D1	++++	++++	++	+++	++++	++++	+++	+++
Fungus D3	++++	+++	+	+	++++	+++	+	+
Fungus D6	++++	++++	++	++++	++++	+++	++	++
Fungus D7	++++	++++	+++	+++	++++	++++	++++	++++
Fungus D8	++++	++++	++++	++++	++++	++	++	++
Fungus D9	++++	+++	+++	+++	++++	++++	+++	+++
Fungus D10	++++	++++	++	+++	++++	++++	+++	+++
Fungus D12	++++	++++	+++	+++	++++	++++	+++	+++
Fungus D13	++++	+++	+++	+++	++++	++++	+++	+++
Fungus D14	++++	Trace	+++	++++	++++	++++	++++	++++
Fungus D15	++++	Trace	+	+++	++++	++++	++	++++
Fungus D16	++++	++	++	++	++	+++	++	++
Fungus D17	++++	++	+++	++++	++++	+++	++	++
Fungus D18	++++	+++	++	++	++++	+++	++	++
Fungus D19	++++	Trace	+	++	++++	++++	+++	++++
Fungus D20	++++	++++	++	++	++++	+++	++	++
Fungus D21	++++	++++	++	++	++++	++++	+++	+++
Fungus D22	++++	Trace	Trace	++++	++++	++++	+++	++++
Fungus D24	++++	++++	+++	+++	++++	+++	+++	+++
Fungus D25	++++	++++	+++	++++	++++	++++	++++	++++
Fungus D26	++++	+++	+++	+++	++++	+++	++	++
Fungus D27	++++	+++	++	++	++++	++++	++++	++++
Fungus D28	++++	+	++	+++	++++	++++	++	+++
Fungus D29	++++	+	Trace	+++	++++	++++	+	+++
Fungus D30, strain 1	++++	+++	+++	+++	++++	+++	++	++
Fungus D30, strain 2	++++	+	+++	+++	++++	++++	+++	+++
Fungus M1	++++	++++	+++	+++	+++	++++	+++	+++
Fungus M2	++++	++++	+	++	++++	++++	++++	++++
Fungus M3	++++	+++	++	++	++++	++++	+++	+++
Fungus M4	++++	Trace	+++	+++	++++	++++	++++	++++
Fungus M5	++++	++	++	++	++++	++++	++	++
Fungus M6	++++	+++	++	+++	++++	++	+	+
Fungus M9	+++	++	+	++	+++	++++	++++	++++

TABLE 5—*Concluded*

FUNGUS	PEPTONE-DEXTROSE AGAR					GLUCOSE-NITRATE-SOIL-EXTRACT AGAR		
	Plain	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Streptomycin (30γ/ml.)	Plain	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
Fungus M10	++++	0	++	+++	++++	+++	+	+++
Fungus M11	++++	+++	+++	+++	++++	++++	++++	++++
Fungus M12	++	0	Trace	+	++	++++	++++	++++
Fungus M13	++++	+	++	+++	++++	++++	+++	+++
Fungus M14	+++	Trace	+	+++	+++	++++	++++	++++
Fungus M15	++++	+++	+++	+++	+++	+++	+++	+++
Fungus M16	++++	++++	+++	+++	++++	++	+	+

* 0 = no apparent growth; + = very poor growth; ++ = fair growth; +++ = good growth; ++++ = excellent growth.

plus 30 γ per milliliter of streptomycin exerted a similar influence. Streptomycin alone had virtually no effect on growth of the fungi. Only 4 cultures appeared to be slightly retarded by its presence.

In glucose–nitrate–soil-extract agar, rose bengal and rose bengal plus streptomycin produced an effect similar to that in the peptone-dextrose agar, except that the development of slightly fewer fungi was reduced.

Seven cultures of fungi grew poorly on plain glucose–nitrate–soil-extract agar but made excellent growth on plain peptone-dextrose medium. On the other hand, 1 culture grew poorly on plain peptone-dextrose medium and very vigorously on the glucose–nitrate–soil-extract agar.

Spore suspensions of the fungus cultures that failed to develop or that grew poorly on one or more of the media named in table 5 were diluted and plated in replicas of four on the same media. After incubation, the apparent number of spores in the original suspensions was calculated (table 6). On acidified peptone-dextrose agar, 12 cultures failed to produce colonies. An additional 5 cultures produced reduced numbers of pinpoint colonies upon prolonged incubation, and probably would be overlooked in a regular soil plating. On the same medium containing rose bengal, 1 culture failed to produce colonies, and 4 cultures produced pinpoint colonies upon prolonged incubation. On the medium containing rose bengal and streptomycin only 2 cultures were affected sufficiently to reduce the number of colonies and to allow only growth of pinpoint colonies after a relatively long incubation period. The results with glucose–nitrate–soil-extract agar were similar to those with peptone-dextrose agar.

The relative rate of spreading of *Trichoderma lignorum*, *Rhizopus nigricans*, and *Cunninghamella bertholletiae* on the various media was tested. All media containing rose bengal slightly retarded the spreading of *C. bertholletiae* and very markedly reduced the rate of growth of the other two fungi.

TABLE 6

Comparative counts of spore suspensions of soil fungi on various media with and without acid, rose bengal, and rose bengal plus streptomycin

FUNGUS	NUMBER OF FUNGI IN THOUSANDS PER ML. OF SPORE SUSPENSION						
	Peptone-dextrose agar				Glucose-nitrate-soil-extract agar		
	Plain	H_2SO_4 (pH 4)	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)	Plain	Rose bengal (1:15,000)	Rose bengal (1:30,000) + Streptomycin (30γ/ml.)
Acrostalagmus cinnabarinus	29	0	31	27	29	30	27
Acrothecium robustum	3	3	3*	3	3	3	4
Aspergillus ochraceus	58	59	64	56	61	51	62
Chaetomium sp.	79	0	88	81	77	77	75
Circinella sp.	95	47*	99	100	87	83	94
Fusarium sp. 6	128	0	130	122	107	122	134
F. sp. 9	83	0	82	91	98	78	94
Hormodendrum pallidum	116	90	92*	83	93	94	97
Monilia pruinosa	10	9*	9	11	7*	6*	6*
Monotospora brevis	3	3	3*	4	3	3	3
Oospora variabilis	67	63	66	72	49*	50*	49*
Penicillium variabile	181	190	120	191	183*	182*	174*
Phoma sp.	4	4†	0	4	6	5	5
Rhizopus nigricans	14	13	15	14	13*	11*	12*
Spicaria divaricata	18	19	19	20	13*	13*	15*
Stysanus stemonites	8	0	11	8	8	7	8
Thieleviopsis basicola.	14	8	15	18	—‡	—‡	—‡
Fungus D3	6	6	5	4	5	6	4
Fungus D6	4	4	4	4	4	3	4
Fungus D8	21	22	23	22	22	20	21
Fungus D14	7	3†	7	7	7	6	7
Fungus D15	6	0	7	8	7	7	8
Fungus D17	4	3	3	3	4	5	5
Fungus D19	13	1†	14	19	15	12	16
Fungus D22	10	0	3†	7†	8	7	9
Fungus D28	91	0	86	88	94	86	85
Fungus D29	8*	0	5†	8*	9	8	8
Fungus D30, strain 1	80	79	81	88	81	78	87
Fungus D30, strain 2	46	47†	46	43	39	41	48
Fungus M2	8	6	<1†	<1†	5	4	6
Fungus M4	102	11†	104	95	92	88	87
Fungus M6	42	46	41	46	51	51	43
Fungus M9	48	52*	45*	47	49	47	48
Fungus M10	94	0	90	84	88	92	89
Fungus M12	9	0	3†	7*	7	7	8
Fungus M13	201	208	207	215	198	202	216
Fungus M14	13*	0	10*	11*	11	10	12

* Poor growth.

† Slow germination; pinpoint colonies; little or no spore formation.

‡ Growth so poor and diffuse that colonies could not be distinguished.

DISCUSSION

Although it is highly improbable that a medium will be found which will prevent the growth of bacteria and actinomycetes and allow the development of all soil fungi, any improvement in the present procedures for determining numbers and kinds of soil fungi would be welcomed by most investigators. The production of antibiotics and the work of Smith and Dawson (4) and of Littman (3) have opened the way for definite progress in this respect. The present paper reports a study of the use, in suggested and new combination, of several of the recently proposed substitutes for acid in fungus media, for preventing bacterial growth and in other ways improving the media.

Littman's oxgall agar containing 1:100,000 crystal violet and 30 γ per milliliter of streptomycin proved to be an excellent medium for determining total numbers of fungi. The growth of some forms is retarded so greatly, and the color is so intense, however, that a considerable proportion of the colonies must be transferred to other media before identification can be made. The substitution of 1:30,000 rose bengal for the crystal violet improves the medium in this respect. In either case the oxgall agar has no particular advantage over the less concentrated peptone-dextrose agar containing rose bengal and streptomycin.

Rose bengal used alone in a concentration of 1:15,000, as proposed by Smith and Dawson, was very effective in reducing spreading and in decreasing the size of the majority of fungus cultures tested. Of 117 fungi, only 5 made extremely poor growth in presence of this dye. The forms affected were found only occasionally and always in very small numbers in the soils used for these studies. On plates containing 1:15,000 rose bengal, very few bacterial colonies developed from some soils; from other soils moderate numbers grew; and from still others such large numbers developed that the growth of some fungi was prevented. Inasmuch as Smith and Dawson did not encounter this difficulty, it would appear that many of the soils of southern California contain larger numbers of bacteria tolerant to rose bengal than do the eastern soils used by those investigators.

Most bacterial colonies were larger on glucose–nitrate–soil-extract agar (see figure 1) than on peptone-dextrose agar. In general, the numbers of bacteria capable of producing colonies on soil-dilution plates containing either agar with 1:15,000 rose bengal were similar. These observations differed from those of Smith and Dawson, who found that bacterial numbers and size of colonies were larger on the peptone-dextrose medium. This possibly indicates that the types of bacteria in the soils used are different, or that the soil extracts differ.

Streptomycin alone allowed relatively large numbers of bacteria to develop on the plates and failed to reduce spreading. For most soils tested, it was necessary to use a combination of rose bengal and streptomycin to obtain the desired results. The addition of 30 γ per milliliter of streptomycin to the media containing 1:15,000 rose bengal virtually eliminated all bacterial growth on dilution plates from most soils. The concentration of the dye was reduced to 1 part in 30,000, with almost equally favorable results. Occasionally, a soil was found which gave a few bacterial colonies. No soils have yet been encountered, however, which contained enough bacteria capable of developing on this medium to interfere with or reduce fungus counts. Identification of fungi was less difficult on the agar containing only 1:30,000 rose bengal.

Although glucose–nitrate–soil-extract agar containing rose bengal and streptomycin proved to be an excellent medium, the peptone-dextrose agar containing the same materials gave somewhat more satisfactory results. This conclusion is based on the tendency of the few bacterial colonies that occasionally developed, and of some of the fungus species, to form larger colonies on the glucose-nitrate medium.

In plating some soils, the only advantage of using rose bengal and streptomycin in place of acid was the reduction in size and spreading of a number of the fungus colonies. In these soils very few or no species of fungi were found which would grow on the rose-bengal–streptomycin medium and not on the acid agar. In most of the soils, however, a small to large proportion of the colonies developing on the rose-bengal–streptomycin medium were types which would not grow on the acid medium. In platings of these soils, total numbers of colonies were often much lower on the acid medium, ranging from slightly reduced numbers to less than half the number developing on the rose-bengal–streptomycin medium. Of 117 cultures tested, 11 failed to grow or produced only a trace of growth when streaked on acid peptone-dextrose agar, and 8 cultures grew very poorly. When spore suspensions of these same 19 cultures were plated, 12 failed to form colonies, and 5 produced reduced numbers of pinpoint colonies upon prolonged incubation on the acid agar. These would probably be overlooked on regular soil plates for fungus determinations. Of these 17 fungi, 6 were isolated in relatively high concentration from one or more soils, and 4 of these fungi constituted a large part of the fungus population of many soils. *Stysanus stemonites*, for example, has been encountered only twice in thousands of platings of southern California soils on acid agar. By use of the same medium with rose bengal and streptomycin in place of the acid, this species has been isolated from nearly all soils plated and has accounted for 20 to 36 per cent of the fungus colonies in some samples.

The substitution of rose bengal and streptomycin for sulfuric acid in fungus agar has thus increased the kinds of fungi isolated by approximately 14 per cent and has increased numbers as much as 100 per cent. It appears that the greater part of the increased count is due to development of types which are sensitive to the acid. Part of the increase is undoubtedly caused by the reduction of spreading and of rapid growth of many cultures by the rose bengal.

As a result of this investigation, peptone-dextrose agar containing 1:30,000 rose bengal and 30 γ per milliliter of streptomycin is now used in this laboratory for new studies involving soil plating for the determination of numbers and kinds of soil fungi. For investigations already under way, in which acid agar was used at first, both media are now employed. Should soils be encountered which contain relatively large numbers of bacteria capable of growing on the rose-bengal–streptomycin medium, it may be possible to prevent such growth by increasing the concentration of rose bengal.

A disadvantage of the rose-bengal medium, in comparison with the acid medium, is that the dye makes it a little more difficult to identify some fungi which could ordinarily be identified on the original plates. Until one becomes familiar with the growth characteristics of the fungi commonly encountered in the soils of an area, it is therefore necessary to transfer more colonies to other media than when using the acid medium.

The chemical and physical properties of streptomycin, as compared with other common antibiotics (7), make it especially favorable for use as a bacterial growth inhibitor in fungus agar. The cost is low, and a sterile solution can be stored in the refrigerator for several months. To prevent destruction by heat, the streptomycin is added to the medium just before the plates are poured, as is the usual practice when adding acid to fungus media.

SUMMARY

A study was made of the comparative use, singly and in various combinations, of acid, rose bengal, and streptomycin as bacterial growth inhibitors in various fungus media for determining numbers and kinds of soil fungi by the dilution plate method.

A concentration of 1:15,000 rose bengal in glucose–nitrate–soil-extract agar, peptone-dextrose agar, and peptone-dextrose-oxgall agar prevented growth of most bacteria in some soils. Other soils, however, contained relatively large numbers of bacteria capable of developing on media containing rose bengal alone. In many instances fungus counts were significantly lowered. A combination of 1:15,000 or 1:30,000 rose bengal and 30 γ per milliliter of streptomycin in all three media, and a combination of 1:100,000 crystal violet and 30 γ per milliliter of streptomycin in the oxgall medium, virtually eliminated bacterial growth from all soils tested. Streptomycin alone had a slightly inhibiting effect on only 2 of 117 cultures of fungi; rose bengal had little effect other than in reducing the size of the colonies.

On the basis of ease of identification of the fungi, size of the few bacterial colonies that occasionally developed, numbers and kinds of fungi, and size of the fungus colonies, peptone-dextrose agar containing 1:30,000 rose bengal and 30 γ per milliliter of streptomycin was rated the best medium for soil-fungus plating. By use of this medium, the numbers of fungi found in the soil were increased as much as 100 per cent, and the kinds of fungi isolated from a relatively large number of samples were increased by approximately 14 per cent, in comparison with those found by use of the same base medium containing acid. Most of the increase in numbers resulted from growth of types of fungi that would not develop on the acid medium, and part of the increase was caused by a reduction in spreading and size of many fungus colonies. Six fungi that were consistently isolated in relatively large concentrations on the new medium were rarely or never isolated on the acid agar (pH 4).

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A VERTICAL SHAKER FOR SEPARATORY FUNNELS

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Many methods for determining minute quantities of certain elements involve use of an organic reagent that reacts with the element in question. The compound thus formed is soluble in some organic liquid virtually immiscible with water. When the aqueous solution of the compound is vigorously shaken with the organic liquid, the element in question is thereby concentrated and isolated from the mass of water and dissolved material. The volume of such work required in some analytical procedures involves so much shaking as to make a mechanical shaker virtually mandatory. Such a shaker, when made to simulate the best manual shaking, saves time, relieves the analyst of much arduous work, and makes possible a standardized uniform shaking not obtainable by hand method. The mechanical shaker described here is highly efficient, since it may be set to run at a uniform rate for a definite time. This provides the thorough shaking essential for accurate results.

Extracts for determining copper, lead, and zinc in soils and plants by the dithizone (diphenylthiocarbazone) system (1, 2) can be prepared best with a mechanical shaker. The apparatus described here has been found to be well adapted for use in making these determinations. It is useful in a wide variety of methods involving two mutually immiscible liquids. Other special applications in which it has been used at this station include: (*a*) separation of inorganic phosphorus in plant material by the general procedure of Pons and Guthrie (3), (*b*) use in certain steps of the colorimetric determination of DDT (2,2-bis p-chlorophenyl 111-trichloroethane) (4), (*c*) hastening dispersion of soil colloids in kinetic equilibrium and sedimentation studies; in this work test-tubes were used as containers and were mounted in an improvised holder fastened to the back of the panel.

The requisites of the shaker are that it hold, in an inverted position, six or more Squibb type separatory funnels of 125-ml. capacity, and shake them with a stroke of about 2 inches at a rate of approximately 300 strokes per minute. The panel may be equipped to hold other containers, and the stroke may be easily adjusted between 0 and 4 inches.

Figure 1 is a working drawing of the shaker with mounted inverted separatory funnels. The numerals refer to the parts described in table 1. The funnels are mounted on shelf 25, and are held firmly in place against the momentum of the stroke by bracket 27. The stopper is kept pressed in the funnel by bracket 28. It is essential that there be more tension on brackets 27 and 28 so that the funnel will be held firmly against the seat of shelf 25. It is also important that the

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[1] The authors are grateful to E. S. Shipley, mechanic in the instrument shop of the Division of Soil Management of Irrigation, for the fabrication and assembly of materials used in construction of this shaker.

TABLE 1

Bill of materials for vertical shaker

PART NO.	NUMBER REQUIRED	NAME OF PART	MATERIAL	REMARKS
1	1	Stand	1½″ x 1½″ x ⅛″ angle iron	16⅝″ wide, 7¾″ high, 30″ long
2	1	Motor		⅛ H.P.—1,725 r.p.m.
3	1	Driving pulley-V type		2½″ O. D.
4	1	Driven pulley-V type		12″ O. D.
5	1	"V" belt		60″ long
6	1	Shaft	Steel	
7	1	Collar	Steel	
8	2	Pillow block	Steel	
9	2	Sleeve bearing	Bronze	
10	1	Slotted disc for adjustable eccentric pin	Steel	
11	1	Eccentric pin, bolt, and nut	Steel	
12	1	Stop screw		
13	1	Washer	Steel	1⅝″ x $\frac{11}{16}$″ x ⅛″
14	1	Crank pin sleeve	Steel	
15	1	Connecting rod	Steel	
16	1	Crank pin bearing	Bronze	
17	1	Crosshead bearing	Bronze	
18	1	Crosshead pin and nut	Steel	
19	1	Washer	Steel	1½″ x $\frac{11}{16}$″ x ⅛″
20	1	Crosshead bar	Steel	11¾″ x 2″ x 4″
21	1	Crosshead panel frame	1″ x 1″ x $\frac{1}{16}$″ Angle iron	
22	2	Guide posts and nuts	Steel	¾″ D x 28″ long, threaded ¾″ each end for ½″ S.A.E., std. nuts
23	4	Runners	Fiber	
24	1	Panel	Wood 11½″ x 19″	Fastened into frame with screws
25	1	Shelf	Wood 11½″ x 2½″ x ⅞″	Fastened to panel with screws
26	1	Shelf	Wood 11½″ x 2½″ x ⅞″	Fastened to panel with screws
27	7	Brackets	Spring, bronze	0.045″ thick
28	7	Stop brackets		
29	3	Braces for guide posts	½″ x ⅛″ Angle iron	Cut to fit, flattened, drilled

brackets be adjusted to permit easy removal of the funnels. The bronze brackets may be chromium-plated; if not, they should be kept covered with a resistant laquer, otherwise the bronze becomes corroded and is likely to contaminate samples with copper and zinc. Bracket 26, which holds the stopper in place, should be cushioned with a tightly fitting sleeve of rubber tubing, the outer end of which is sealed. The end of the tubing may be sealed by applying rubber

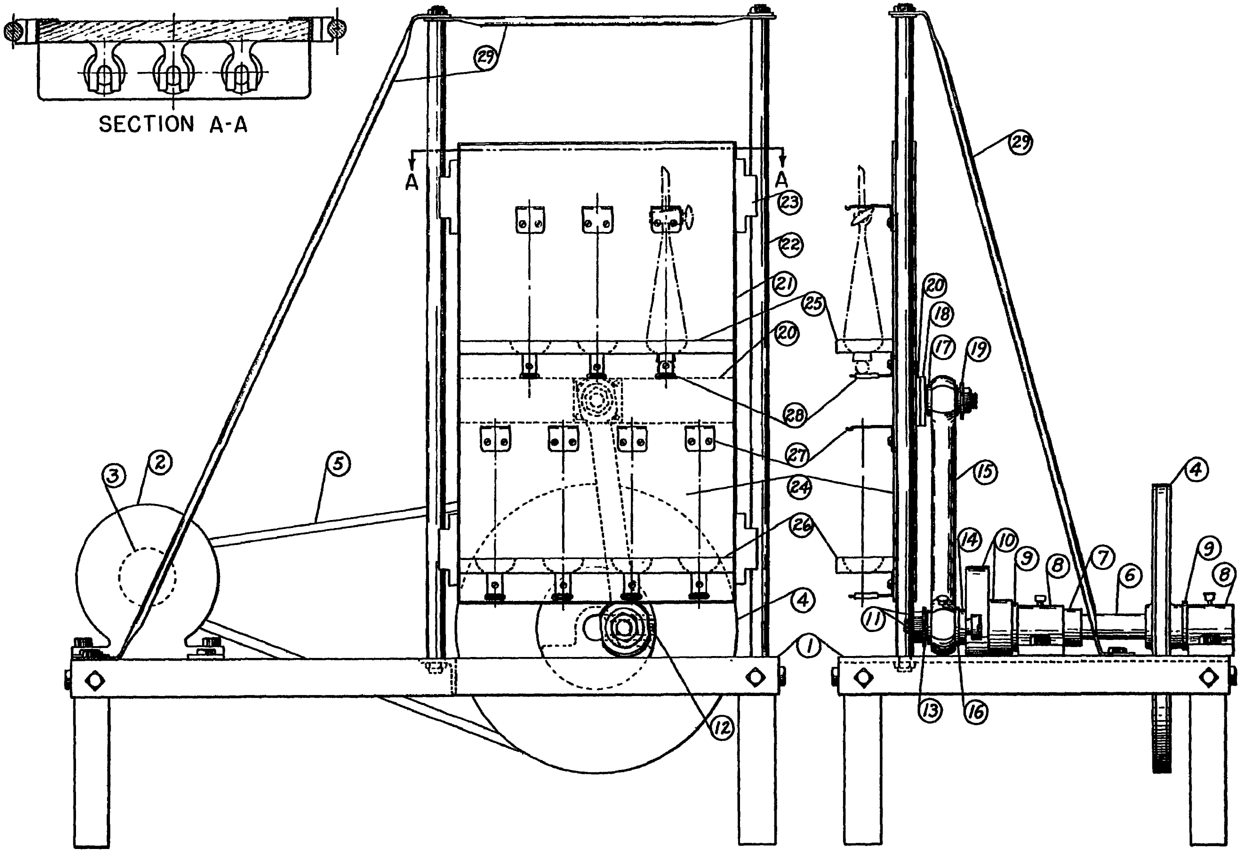

FIG. 1. VERTICAL SHAKER WITH MOUNTED INCERTED SEPARATORY FUNNELS

Numbers refer to parts described in table 1.

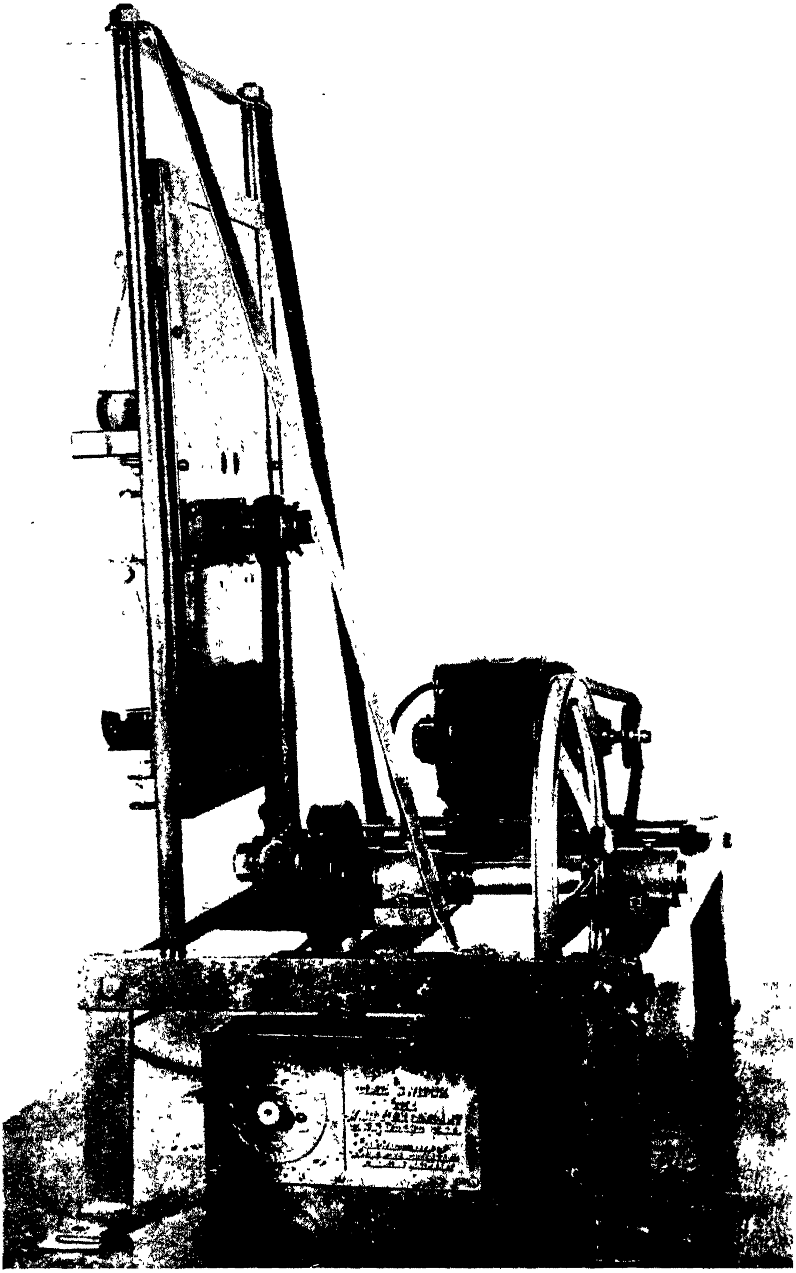

FIG. 2. SIDE VIEW OF THE ASSEMBLED SHAKER WITH TIME SWITCH

cement within the end of the tube and placing it in a Hoffman clamp overnight. Figure 2 shows the assembled apparatus with time switch. Any good automatic time switch should be satisfactory.

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COPPER AMALGAM ELECTRODE AND ITS APPLICATIONS: I. CONSTRUCTION AND CALIBRATION OF THE ELECTRODE[1]

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One of the promising methods for study of soil, plant, and other biological systems involving trace elements is measurement of ion activities. The complications which might arise are so numerous, however, that each individual case deserves detailed investigation before the usefulness of any one technique can be generally accepted or discounted. As the importance of copper in most biological systems has been recognized, the possibilities of determining cupric-ion activities in such systems and of correlating the results with known chemical and biological behavior have been explored.

Many previous investigators have used two-phase copper amalgam electrodes for studying the activity coefficients of pure copper solutions and determining the standard potential of copper. Such works have been ably summarized by MacInnes (11), but no one has further investigated the possibilities of the copper amalgam electrode. Even the properties and behavior of the amalgam itself have been little studied. Nielsen and Brown (14) used a two-phase copper amalgam and reported that its potential is independent of the relative quantities of copper and mercury within wide limits. Newberry (13) has reported that the potential between pure copper and two-phase copper amalgam is zero. Lewis and Lacey (8) concluded that oxidation in the copper electrode owing to the presence of air plays no important role, as shown by the fact that similar results could be obtained in both presence and absence of oxygen. Luther and Wilson (10) have found that no special precautions are needed against atmospheric oxidation at the copper electrode. They reported the equilibrium constant value for $\frac{Cu^{++}}{(Cu^{+})^2}$ in the presence of metallic copper at 25°C. as 1.5×10^6. These reports from earlier literature indicate the possibility of using a two-phase copper amalgam for the measurement of cupric-ion potentials without resorting to tedious precautions.

The purpose of this paper is to describe the construction of a two-phase copper amalgam electrode and to show its applicability to a study of the activity of copper in soil systems.

MATERIALS AND METHODS

Preparation of the amalgam

Triple distilled mercury and sheet electrolytic copper of high purity were used in preparing the amalgam by electrolysis. The electrolytic vessel consisted of a tall 600-ml. pyrex beaker of about 40 sq. cm. cross-sectional area. Into the beaker was poured 100 ml. of mercury, which formed the cathode pool. A half-molar solution of copper sulfate, acidified with sulfuric acid to a value between pH 3.0 and 4.5, was poured over the mercury as the conducting medium. A copper anode of about 30 sq. cm. was dipped into this solution. Electrical contact with the mercury cathode was made by means of a platinum electrode dipped into the pool. A current density of about 5 amperes per square decimeter of mercury was used. Stirring the mercury with a motor-driven stirrer during the electrolysis is advantageous because it decreases the tendency to form a lumpy amalgam. The exact strength of the copper amalgam is immaterial, as discussed later in this paper, but a 1 to 2 per cent amalgam is satisfactory from all points of view. Higher concentrations tend to give frequent troubles in handling and manipulation of the electrode. The amalgam was washed with copper sulfate solution, the strength of which seems to be unimportant, although Adams and Brown (1) used a copper sulfate solution of specified strength for washing the amalgam, as have all subsequent investigators.

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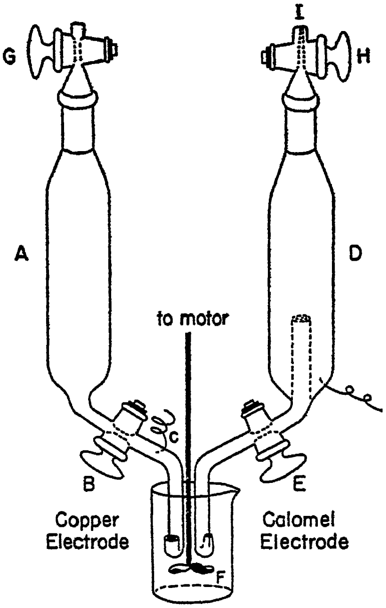

FIG. 1. DIAGRAMMATIC SKETCH OF COPPER AMALGAM ELECTRODE

Description of electrode

A diagrammatic sketch of the electrode used is given in figure 1. *A* is an amalgam reservoir made of Pyrex glass and of any desired capacity. A tube of 5 mm. outside diameter is sealed to the lower end of the reservoir and bent as shown in the diagram. By opening stopcock *B*, the drops of amalgam can be renewed at will. At *C* below the stopcock, is a tungsten contact which provides electrical connection with the amalgam. *D* is a saturated calomel half cell, the salt-bridge arm of which is drawn into a fine capillary at the free end and bent upward as shown. This is to prevent mixing of the solution from the beaker with the KCl. By opening stopcock *H* occasionally, any particles that clog the capillary can be driven out and the KCl contact renewed. Above stopcock *H* the tube is drawn into a capillary to prevent excessive flow of KCl solution when the stopcock is opened momentarily. This would often be necessary when making readings on suspensions of clays and organic matter. Stopcock *E* must be kept open when making measurements. A beaker containing the solution or suspension is brought below the electrode on an adjustable stand. A motor-driven stirrer *F* is used to stir the suspension. By careful construction of the electrode, it is possible to make measurements on small volumes of solutions contained in 15- or 20-ml. beakers. In soil and plant work, use of a 50- or 100-ml. beaker is convenient.

The tube of the amalgam reservoir is first filled by dipping the free end under amalgam in a beaker, opening stopcock *B*, and pulling air through *G*. The reservoir is then filled with amalgam by pouring it through the ground glass opening at the top. A thin layer of copper sulfate solution is poured over the amalgam, which protects it from deterioration due to atmospheric contact. It is advisable to filter the amalgam through capillary tubing before introducing it into the electrode. This setup is stable for several months.

An ordinary student's potentiometer was used to make potential readings and a galvanometer of sensitivity 0.5 mv. for indication of null point. Higher degrees of precision are unwarranted in such systems because of the uncertainty of liquid junction potentials.

The spent amalgam was recovered by elutriation with water. Pure mercury was recovered from this collected bulk by stirring under a solution of dilute HNO_3 and $HgNO_3$ for 3 days, washing through dilute KOH and distilled water in long columns, and distilling three times under high vacuum, maintaining a still surface. This purified mercury could be used over again, with practically no waste.

Cell Arrangement

Measurements were made on the following cell:

$$\mathrm{Hg};\ \mathrm{Hg_2Cl_2(S)},\ \mathrm{KCl(sat.)}::\ \mathrm{Cu^{++}};\ \mathrm{(Hg)\ Cu}$$

The copper electrode reaction is $Cu^{++} \rightarrow Cu$. The potential of the cell is given by the equation.

$$E = E_0 - \frac{0.059}{2} \log \frac{1}{(\mathrm{Cu^{++}})}$$

In this equation (Cu^{++}) represents cupric-ion activity on the molal scale, E_0, the standard potential of the cell and E, the total potential of the cell. E_0 has the value 0.099 volt (3).

Cupric-ion activities were expressed as pCu values, which are defined as minus $\log_{10}$ of active cupric-ion molality. For a solution of copper sulfate, it is minus $\log_{10}$ of the cupric-ion molality multiplied by its activity coefficient.

EXPERIMENTAL RESULTS

Measurements of cupric-ion activities in pure copper solutions

Standard solutions of copper salts were prepared with Pyrex-distilled water. The potentials of these solutions were compared with the calculated values obtained by using activity coefficients reported by Lewis and Randall (9). The results obtained are given in table 1. It is seen from these that the observed potentials agreed within 2 or 3 mv. of the calculated values, which is well within liquid-junction errors. It is clear from these results that the standard potential of the amalgam is the same as that of pure copper metal.

TABLE 1

Results of measurements with standard copper solutions

SALT	MOLALITY	IONIC STRENGTH	ACTIVITY COEFFICIENT	*E* Observed	*E* Calculated	*E* Deviation
				mv.	*mv.*	*mv.*
$CuSO_4$	0.00025	0.001	0.78	−8	−10	2
	0.0025	0.01	0.60	19	16	3
	0.005	0.02	0.53	25	23	2
	0.0125	0.05	0.43	35	33	2
	0.025	0.1	0.34	40	38	2
$CuCl_2$	0.0003	0.001	0.78	−6	−7	1
	0.003	0.01	0.60	18	18	0
	0.006	0.02	0.53	29	27	2
	0.016	0.05	0.43	39	36	3
	0.033	0.1	0.34	41	40	1
$Cu(NO_3)_2$	0.0003	0.001	0.78	−5	−7	2
	0.033	0.1	0.34	41	40	1
Mixture of above three	—	0.0009	0.78	−7	−9	2

Activity measurements on complex copper salts and insoluble copper compounds

The cupric-ion activities of several copper compounds were measured by means of the electrode. The reliability of the readings was tested from time to time by checking the electrode against a standard solution of copper sulfate, 0.025 *M*, which has a potential between 38 and 40 mv. at room temperature. Several readings were obtained by repeated new drops of amalgam, and all of the readings agreed within 2 or 3 mv. The potential readings were converted into pCu values (−log. molal activity of cupric ions) and are presented in table 2.

Verification of electrode readings in presence of diverse ions and proof of applicability to complex inorganic systems

The ability of the electrode to read cupric-ion activity in pure solutions of copper is no indication of its dependability when applied to complex systems such as soils and plants. A series of checks were therefore made to test the reliability of the electrode under such conditions and to determine interferences from various sources at the electrode surface.

TABLE 2

Activity of complex copper salts and insoluble copper compounds

COMPOUND	MEASURED pCu VALUE	pCu VALUE CALCULATED FROM OTHER DATA
CuS (suspension)	17.6	18; 18.75
CuO (suspension)	11.6	
Cupric oxalate (saturated solution)	6.0	
$CuCO_3\ (CuOH)_2$	2.7	
Cu-alanine (solution)	4.0	
$Cu\text{-}Na_2S_2O_3$ (solution)	>20	
Humic acid (Merck) (suspension)	6.4	
Cupric hydroxide (suspension)	6.8	6.4
Cupric-amines of ammonia		
Ordinary distilled water	6.4 to 6.8	
Pyrex-distilled water	8.8	7.6

To test for interference from anions and cations commonly present in peat, the following procedure was used. Two different peats were selected, one with low soluble salts and the other with an abnormally high soluble salt content. A 1:10 soil-water extract was then prepared. To the filtered soil-water extract was added a measured quantity of copper sulfate solution of which the molality and ionic strength were known. The quantity of soil extract used was varied to give different dilutions, the molality and ionic strength of copper sulfate in the final solution being kept constant. It was thus possible to obtain a series of solutions in which the molality of copper added remained the same but the amount of soil ions present varied in definite proportions. The following example illustrates the procedure:

SOIL EXTRACT	0.005 M $CuSO_4$ SOLUTION	WATER	CONCENTRATION OF SOIL IONS AS FRACTION OF ORIGINAL
ml.	*ml.*	*ml.*	
25	25	0	$\frac{1}{2}$
10	20	10	$\frac{1}{4}$

By measuring the potentials of such a series of solutions, calculating the activity coefficients of copper in each case, and applying the limiting Debye-Hückel equation for systems containing multivalent ions, the ionic strength contributed by the soil ions in each case was found. The values in moderately dilute concentrations were accepted as reliable, and the various values of ionic strength obtained were compared. Obviously, for every dilution of the soil extract to half the concentration, the ionic strength is reduced to half the previous value. If the ionic strengths calculated from the observed cupric potentials bear this simple relationship, within the limits of experimental error, it is an indication that the potential has varied only as a function of the ionic strength of the solution and that no interference from any ions or groups of ions has occurred at the electrode surface to vitiate the cupric potential.

TABLE 3

Test for interference from soil ions

CONCENTRATION OF EXTRACT AS FRACTION OF ORIGINAL	*E* OBSERVED	ACTIVITY OF COPPER (fM)	ACTIVITY COEFFICIENT OF COPPER (f)	TOTAL IONIC STRENGTH OF SOLUTION	IONIC STRENGTH OF SOIL EXTRACT
*Low-salt peat extract**					
	mv.				
1/2	−5	2.9×10^{-4}	0.11	0.22	0.21
1/4	1	5×10^{-4}	0.19	0.12	0.11
1/8	8	7.8×10^{-4}	0.31	0.06	0.05
1/16	12	1.1×10^{-3}	0.44	0.03	0.02
1/32	14	1.3×10^{-3}	0.50	0.02	0.01
*High-salt peat extract**					
1/2	−5	2.9×10^{-4}	0.11	0.22	0.21
1/4	−33	3.1×10^{-5}	0.012	1.02	1.01
1/8	−20	9.4×10^{-5}	0.037	0.51	0.50
1/16	−5	2.9×10^{-4}	0.11	0.22	0.21
1/32	1	5×10^{-4}	0.19	0.12	0.11

* Concentration of added copper was maintained at 0.0025 *M* at all dilutions.

The Debye-Hückel equation for multivalent ions states that $-\log f = z^2 A\sqrt{m}$, where f is the activity coefficient of the ion in question, z its valence, m the ionic strength, and A is constant for the particular solvent employed. Comparing ratios of the values for ionic strength obtained from the preceding equation with those expected from dilution ratios for the soil extract indicates the accuracy of the electrode readings. The results obtained are contained in table 3 and figure 2.

These results show that for every dilution to half the concentration, the ionic strength as calculated from the observed potentials has decreased almost exactly by half. The negative logarithms of the activity coefficients when plotted as a function of the square root of ionic strength give a straight line (fig. 2), indicating conformity to the Debye-Hückel equation. The only exception is in the case of the high-salt peat at a very high concentration of soluble salts. This discrepancy is accounted for by the deviation of the Debye-Hückel equation at such high concentrations. The electrode, therefore, should give reliable readings of cupric-ion activity in the presence of soluble organic matter and other diverse ions commonly encountered in peats where abnormal amounts of soluble salts are not present.

Interference from other sources

It can be expected from theoretical considerations that the noble metals, like gold, silver, and platinum, and other metals like palladium and tellurium would interfere with cupric-ion activity determinations. The quantity of these metals and many others which can be tolerated by the electrode was checked. The electrode reading in a typical peat soil suspension was noted, and successive quantities of these various materials were added with constant stirring until a shift in the potential reading occurred. The results are presented in table 4. Platinum and mercuric mercury are the two seriously interfering ions, but it is extremely unlikely that they are present in any soil in amounts sufficient to vitiate the cupric potentials. All other ions tested are of no especial significance so far as their possible interference in soil and plant work is concerned. The case

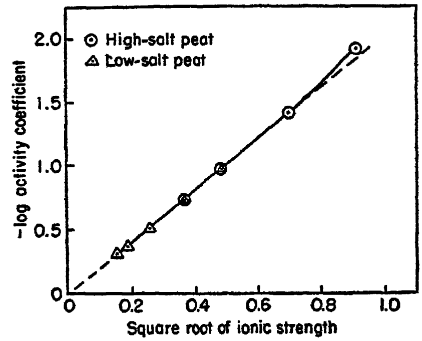

FIG. 2. VERIFICATION OF ELECTRODE READINGS IN PRESENCE OF DIVERSE IONS BY MEANS OF DEBYE-HÜCKEL EQUATION

TABLE 4

Effect of various ions on the cupric potential of peat

METAL ION ADDED	ME./100 GM. OF SOIL, REQUIRED TO CHANGE ORIGINAL READING	METAL ION ADDED	ME./100 GM. OF SOIL, REQUIRED TO CHANGE ORIGINAL POTENTIAL READING
Platinum	2	Cobalt (ous)	>100
Gold	10	Nickel	>100
Palladium	10	Zinc	>100
Tellurium	6	Manganese (ous)	>100
Silver	10	MnO_2	250
Mercuric mercury	0.5	Ferrous iron	>100
Cadmium	>100	Ferric iron	45

of ferric iron deserves special attention, however, as most soils might contain appreciable quantities of this element. Ferric iron interference is indicated by very highly positive readings, great instability, and a complete breakdown of the electrode. The effect is pronounced in the presence of chloride. Mercury undergoes oxidation to the mercurous state, and the ferric iron undergoes reduction to the ferrous state, as shown below.

$$2\,Hg + 2\,Cl \rightarrow Hg_2Cl_2 + 2\,E^+$$
$$2\,Hg + 2\,Cl + 2\,Fe^{+++} \rightarrow Hg_2Cl_2 + 2\,Fe^{++}$$

The ferric iron effect was tested on various peat soils with widely differing iron contents. Results, presented in table 5, show that the amount of ferric iron required to shift the potential readings of many peat soils is very large, and seldom, if ever, will interference occur from this cause in making soil measurements.

TABLE 5

Ferric iron interference with the electrode

SOIL NO.	pH	pCu	QUICK TEST IRON	AMOUNT OF FERRIC IRON REQUIRED PER 100 GM. SOIL TO CHANGE pCu
			lb./A	*me.*
8-1	3.6	8.9	1300	20
38-4	3.6	7.0	1400	15
17-2	3.7	7.4	1	30
4	3.8	8.9	—	45
6-1	4.4	6.4	400	30
59-1	4.4	6.7	50	40
95-1	5.0	6.9	5	40
69-1	5.5	6.7	8	40
37-2	5.8	8.1	2	70
22-4	6.2	9.9	2	65
32-1	6.4	11.5	1	55
20-3	7.4	10.6	2	50
20-6	7.4	10.9	12	45

Acidity limitations

The electrode cannot be used to measure cupric-ion activities in solutions which are above pH 8.5. The readings become unstable, probably because of oxidation of mercury according to the reaction

$$Hg + 2\,OH \rightarrow HgO + H_2O + 2\,E^-$$

For this reason, it is not possible to measure the cupric-ion activity of the complex cupric-ammonia amines by means of the electrode. Acidities up to pH 2 do not cause any interference.

DISCUSSION

General Considerations

The possibilities of the copper amalgam electrode for studies of cupric-ion activity in complex soil and plant systems were investigated. The characteristics of copper amalgam seem to make it an especially useful tool in such studies. The amalgam does not easily deteriorate in air and can be indefinitely kept under a dilute solution of copper sulfate. The exact concentration of a copper amalgam that can give the standard potential of copper has never been investigated by anyone, but our experience has shown that the potential does not vary from that of pure copper even when the concentration of copper in the amalgam does not exceed 0.5 per cent. As the saturated solution of copper in mercury is continuously drained out of the electrode, the upper phase in the amalgam reservoir becomes a semi-solid mass which apparently is a highly concentrated amalgam. When the amalgam assumes this consistency it is too solid to flow through the electrode. Addition of pure mercury and thorough mixing restore its original properties. The authors have been able to use 100 ml. of a 4 per cent copper amalgam in this manner, by successive dilutions with pure mercury, until about 15,000 individual copper activity measurements were made. The spent amalgam can be recovered without appreciable loss and pure mercury obtained by washing and distillation.

The electrode can be standardized before use by measuring the potential of any standard copper solution. We have used a 0.025 M copper sulfate solution, which gives a potential reading of 38 to 40 mv. at room temperature. It is advisable to check the electrode from time to time with this solution when making a large number of determinations. A precision within more than 2 or 3 mv. is unwarranted in such a system because of uncertainties in liquid junction potentials.

When making measurements, time must be allowed to ensure equilibrium and to obtain a constant potential. Usually it does not take more than a few seconds to attain a constant value in the reading. Fluctuating and unstable potentials will be observed if the solution creeps between the amalgam drop and the wall of the glass tube. Instability would result if the solution were a very high pH (say 8.5) or below pH 2. Drops must preferably be renewed before each reading is taken.

The electrical connections have to be checked frequently and the tungsten contacts cleaned with alkali and acid. Before making a series of measurements, it is advisable to check the electrode against a negative standard, besides the positive copper standard mentioned above. In our investigations on soils, we have used a peat suspension adjusted to pH 8.4 with ammonium hydroxide. Such a system is very highly buffered with respect to cupric potential and shows a reading of −405 mv. All peats show this effect, the reasons for which will be discussed in subsequent publications.

Statistical analysis of a large set of data has shown that the error involved in the readings is no larger than ± 0.1 pCu unit.

Activity measurements

Results of activity measurements presented in table 2 bring out many interesting facts. Sodium thiosulfate forms a soluble complex with copper having a very low cupric-ion activity. This complex, however, is unstable and decomposes with precipitation of sulfur. A stable copper complex can be prepared by buffering the thiosulfate solution at pH 4.8 in the presence of sulfurous acid. This complex has an extremely low cupric-ion activity. Such a thiosulate solution is useful in removing the last traces of copper in analytical procedures.

The measured copper activity of cupric sulfide closely agrees with those calculated from solubility product values reported by Kolthoff (6) and Hogness and Johnson (5). The solubility of copper sulfide, 3.3×10^{-4} gm. CuS per liter of water, given in the Handbook of Chemistry (4) is unacceptable and corresponds to an activity of a little greater than pCu 6. That would then equal the copper activity in distilled water. If the CuS were prepared by adding a soluble sulfide to a copper solution followed by thorough washing, and then suspended in distilled water, the copper activity measured is only that of the distilled water. Leibig, Vanselow, and Chapman (7) report a pCu value of less than 8 (0.0006 ppm.) in water distilled from an all-Pyrex set, whereas the high-grade Pyrex-distilled water in this laboratory showed a pCu value of 9 (0.00006 ppm.). A copper sulfide sample prepared in the manner mentioned had a pCu value of 6. If the CuS is prepared by adding a few drops of copper solution to an excess of sulfide solution followed by thorough washing, the CuS would carry with it traces of sulfide ions, which would lower the cupric-ion activity to that of the sulfide. By this method the activity shown by the electrode was pCu 17.6, which closely approximated the values calculated from the solubility products of Kolthoff and Hogness and Johnson. This is additional evidence regarding the accuracy and dependability of the electrode in reading very low values of cupric-ion activity.

The applicability of the electrode to complex ionic systems has been verified by use of the Debye-Hückel equation. Detailed studies on soils and plants have subsequently been made by means of the electrode (2, 12). Figures presented in tables 4 and 5 indicate that interference from any of the several possible sources in soils and plants is extremely unlikely. The tremendous complexing capacity of peat soils for most cations would probably account for the neglibible effect they have on the cupric potential of the system even in the presence of very large amounts of such cations. Within comparatively few limitations, therefore, the copper amalgam electrode appears to have immense potentialities, as in the study of cupric-ion activities in soils, plants, and complex biological systems.

SUMMARY

A two-phase copper amalgam electrode for the measurement of cupric-ion activities was designed and constructed.

The readings in pure copper solutions closely approximate theoretically calculated activity values. The copper amalgam has the standard potential of pure

copper metal over a wide concentration range. It does not deteriorate on standing and can be easily and economically handled.

Activity values for various copper compounds were determined and compared with other published data.

Applicability of the electrode to complex ionic systems has been verified through the Debye-Hückel equation.

Figures are presented to show that reproducible and stable readings with peat soils can be obtained and that interference from many possible sources are not ordinarily likely to occur.

The advantages and limitations of the electrode are discussed.

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KINETIC EXCHANGE STUDIES ON CLAYS WITH RADIOACTIVE CALCIUM[1]

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In studies of cation exchange in soils and clays, it has been assumed that the cations of an element in the solution phase are in kinetic equilibrium with the exchangeable ions of the same element. Before the advent of isotopes that could be used as tracers, this assumption could not be verified by direct experimentation. The direct measurement of the rate of exchange between cations of the same element had to await the availability of isotope tracers. The earliest known example of such work with exchange surfaces was that of Paneth and Vorwerk (11) in which they used Th B, $_{82}Pb^{212}$, to determine the specific surfaces of insoluble lead salts. Kolthoff *et al.* (6, 7) extended the work with this isotope and formulated clear concepts of the surface of $PbSO_4$. Recently, by means of a radioactive isotope of phosphorus, P^{32}, McAuliffe *et al.* (8) studied rates of reaction of phosphorus with several soils having different levels of phosphorus fertility.

Radioactive Ca^{45} is suitable for studies of this nature because of its availability from uranium nuclear reactors and the predominance of calcium among the normal exchangeable bases of soils. Its half-life of 180 days and maximum β radiation energy of about 300,000 electron-volts offer little restriction to its use in laboratory investigations.

The reaction of Ca^{45} with the clay minerals kaolinite, halloysite, hydrous mica, beidellite, and montmorillonite has been investigated. To ensure systems that would involve only exchange of isotopes of one element and not additional chemical exchange between bases, the clays were saturated to pH 7 with calcium prior to addition of Ca^{45}. The investigations involved determination of (*a*) the rapidity of equilibration of added calcium with the exchangeable calcium, and (*b*) the fraction of the solid phase calcium that is in kinetic equilibrium with the solution phase calcium.

MATERIALS

The clays except beidellite were dispersed in water, by addition of ammonia where necessary. The suspensions were passed through a supercentrifuge to remove particles of diameter greater than 0.2μ. Excess water was removed through Pasteur-Chamberland filters by suction. Concentrations of the clay suspensions were determined by weighing after evaporation of the water. The sources of the clays were as follows: kaolinite as English china clay; halloysite as Indianaite from Lawrence County, Indiana; hydrous mica as illite from Illinois; beidellite as the subsoil clay of Putnam silt loam from Missouri prepared by the Department of Soils of the University of Missouri; and montmorillonite as the bentonite Volclay No. 2 from Wyoming.

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[1] Joint contribution from Purdue University, LaFayette, Indiana, and the Division of Soil Management and Irrigation, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, Beltsville, Md. Abstracted from a dissertation submitted by the senior author to Purdue University in partial fulfillment of the requirements for the degree of doctor of philosophy.

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The Ca^{45} was obtained from the Oak Ridge, Tennessee, plant of the U. S. Atomic Energy Commission. Both the regular unit, containing 0.8 millicurie in 10 gm. of Ca as $CaCO_3$, and a high specific activity unit of $CaCl_2$, prepared from a $Ca(OH)_2$ target in which 0.8 millicurie is contained in 33.1 mgm. of Ca, were used.

CaO was made by igniting reagent grade $CaCO_3$ at 1,000° C. for 4 hours. This was placed in water, the solution adjusted to pH 9.0 by addition of glacial acetic acid, filtered to remove Mg, and finally adjusted to pH 7.0 with acetic acid. The calcium acetate concentration was normal.

EXPERIMENTAL PROCEDURES

Rapidity of exchange of Ca^{45} for exchangeable Ca

Aliquots of suspensions of the five clays containing 1 gm. of clay were placed in 50-ml. centrifuge tubes. These suspensions were treated with neutral normal calcium acetate, shaken on an end-over-end shaker for 30 minutes, and centrifuged at 2,500 r.p.m. for 15 minutes. The liquid was decanted for pH measurement, and the solid treated again with calcium acetate. This cycle was repeated until the pH of the solution was 7.0, which was used as the criterion of calcium saturation of the clays.

The clays were washed with 50 per cent ethyl alcohol. After each washing the suspensions were centrifuged, and the wash liquid was decanted. When the wash alcohol gave no precipitate with ammonium oxalate, the clays were washed one additional time. The system was then considered free of excess calcium.

To each tube was added 24 ml. of water. The clays were agitated into suspension, and the tubes shaken in an end-over-end shaker for 48 hours. Then 1 ml. of solution containing 0.1 microcurie of Ca^{45} was added to each tube. This solution was made from high specific activity Ca^{45}; thus the total quantity of added Ca was only about 4 γ, which is considered too small to have any appreciable effect upon the rate or extent of reaction. The tubes were returned to the shaker. Replicate tubes were removed from the shaker at designated times for analysis. Equilibration was at room temperature.

After centrifugation of the tubes at 2,500 r.p.m. for 15 minutes, the supernatant liquid was removed and measured. Differential weighings of the tubes containing the clays before and after heating at 110° C. for 24 hours permitted calculation of the amount of liquid in the system which was not removed. The decanted solution was further clarified by centrifugation at 16,000 r.p.m. in a high-speed centrifuge attachment for 10 minutes. An aliquot of the liquid was used for total Ca determination by precipitation as the oxalate and titration with 0.001 *N* hexaperchloratocerate in a centrifuge procedure (13). An alternate method for small quantities of Ca was the determination by means of picrolonic acid in a colorimetric method of Snell and Snell (14, pp. 466–467).

Enough Ca was added to another aliquot of the solution to bring the total Ca content to 25 mgm. The Ca was precipitated as the oxalate, collected on a filter disc, humidified, and weighed to determine the total Ca. Radioactivity determinations of the Ca^{45} were made with a Geiger-Müller counter. The radioactivity and analytical procedures have been described elsewhere (1). The amount of Ca^{45} on the clay was assumed to be the difference between the Ca^{45} added and that recovered in the solution phase.

Solid phase Ca in equilibrium with added Ca^{45}

These experiments were conducted at 21 ± 1° C. Clays were saturated with Ca, washed with 50 per cent ethyl alcohol, and aliquots of solutions containing various amounts of total and radioactive Ca were added. The final volume of all solutions was 25 ml. The systems were shaken in an end-over-end shaker for 48 hours, and the liquid phase was then removed by centrifugation and decantation. The volume of liquid not removed was determined by weighing the tubes and subtracting the weight of the tube and clay.

The clays were washed with 50 per cent ethyl alcohol until the liquid phase was free of Ca. The exchangeable Ca was replaced by neutral normal ammonium acetate. Total Ca and Ca^{45} analyses were made on the solutions from both phases of the system. The aliquots used for the volumetric Ca determinations were approximately one fourth of the total volume. Calcium oxalate is too soluble to allow accurate analysis of solutions containing very small amounts of Ca. Some of the solutions were analyzed by the picrolonic acid method, which is more sensitive in determining Ca.

RESULTS

Rapidity of exchange of Ca^{45} for exchangeable Ca

Figure 1 shows the ratio of the exchangeable Ca^{45}, Ca(e) to that in the solution, Ca(s), at various times. The intervals represent the elapsed time between addition of Ca^{45} to the clay and the start of the 2,500-r.p.m. centrifugation. Complete equilibration occurs in less than 2 hours. For all clays except hydrous mica, equilibrium was established or virtually so at the first determined interval. These periods are as follows: bentonite, ½ hour; beidellite, kaolinite, and halloysite, 1 hour. Necessary operations of the procedure, such as mixing and centrifugation, require such periods of time that ½ hour is about the shortest interval that can be studied. Once a maximum ratio was reached, all clays except kaolinite, which showed a reduction at between 1 and 2 days, maintained this value.

To confirm this peculiar behavior of kaolinite it was necessary to separate another batch of the mineral. This second equilibration was conducted at 21 ± 1° C. to determine whether the delayed equilibration was caused by a temperature change. Total Ca and Ca^{45} analyses were made on both the solution and exchangeable phases of the system. A graph of the data is shown in figure

1 as "kaolinite 2." The same general type of curve indicates a similar secondary reaction as in the first experiment. Chemical analyses indicated a slight increase in the total Ca of the liquid phase in both experiments with kaolinite after the 24-hour period. Thus the delayed equilibration indicated by the data could be due to hydrolysis of the calcium kaolinite.

The ratio of Ca^{45} on the solid to that in solution is not to be interpreted as a measure of the cation-exchange capacity of a clay. In general, the clays of higher exchange capacities have higher ratios of Ca^{45} on the solid to Ca^{45} in the liquid. The occurrence of varying amounts of calcium in the liquid phase of each clay allows an absolute measurement of the exchange capacity by this method only if the quantity of calcium in the liquid phase is known.

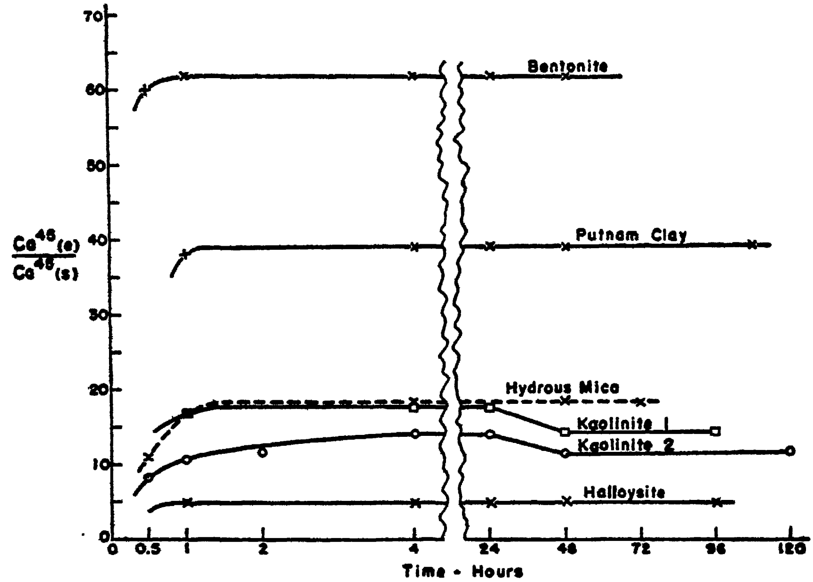

FIG. 1. RAPIDITY OF EQUILIBRATION OF CLAYS AND SOLUTIONS

Solid phase Ca in equilibrium with added Ca^{45}

Results of these experiments are shown in tables 1 to 5. Included are the ratios of the solid phase Ca to that of the liquid phase, and the ratios of the solid phase Ca^{45} to the liquid phase Ca^{45}. These ratios decrease with an increase in total Ca of the liquid phase, because the exchangeable Ca remains approximately constant.

The serious discrepancies between the ratios for the solutions that contained small amounts of Ca are due to analytical limitations. In many cases the small amounts of Ca in these solutions could not be determined satisfactorily even by the picrolonic acid method.

A typical relationship between the logarithms of the ratios is shown in figure 2 for halloysite. The other clays show similar relationship. Deviations from the linear portions indicate the points at which the analytical determination becomes a limiting factor. Extrapolation of the straight portions of the graphs indicates the ratio of Ca(e) to Ca(s) which existed but which could not be determined by chemical analytical methods. The fact that the two ratios are equal with determinable amounts of Ca(s) indicates that they are equal when the amount of Ca(s) is indeterminable. In the latter cases the actual amount of Ca(s) is cal-

TABLE 1

Distribution of Ca and Ca^{45} between exchangeable and solution phases of kaolinite systems

Ca(e)	Ca(s)	$\frac{Ca(e)}{Ca(s)}$	$\frac{Ca^{45}(e)}{Ca^{45}(s)}$	SPECIFIC ACTIVITY	
				Ca(e)	Ca(s)
mgm.	*mgm.*			$\times 10^{-5}$	$\times 10^{-5}$
2.64	0.004	660.0	26.8	3.65	3.63*
2.64	0.013	203.0	18.5	3.59	3.59*
2.64	0.014	189.0	14.6	3.54	3.55*
2.65	0.009†	329.0	14.1	84.7	85.0*
2.64	0.018	147.0	11.3	3.48	3.46*
2.64	0.024	110.0	9.0	3.44	3.44*
2.53	0.148	17.1	12.6	0.895	0.899
3.16	0.230	13.7	7.28	2.88	2.88
2.97	0.900	3.38	3.30	1.18	1.16
2.99	1.16	2.50	2.58	1.87	1.93
3.01	1.07	2.71	2.81	1.90	1.97
2.67	1.05	2.55	2.57	65.5	64.9
2.71	9.24	0.293	0.292	17.7	17.7
2.67	93.7	0.029	0.028	1.88	1.87
2.63	178.0	0.015	0.015	1.04	1.04

* Calculated.

† Determined as calcium picrolonate.

TABLE 2

Distribution of Ca and Ca^{45} between exchangeable and solution phases of halloysite systems

Ca(e)	Ca(s)	$\frac{Ca(e)}{Ca(s)}$	$\frac{Ca^{45}(e)}{Ca^{45}(s)}$	SPECIFIC ACTIVITY	
				Ca(e)	Ca(s)
mgm.	*mgm.*			$\times 10^{-5}$	$\times 10^{-5}$
2.56	0.027	95.7	6.62	3.84	3.84*
2.32	0.015†	15.1	6.03	93.8	93.8*
2.29	1.34	1.68	1.71	1.70	1.73
3.16	2.60	1.21	1.19	0.136	0.135
2.58	3.79	0.681	0.680	5.67	5.67
2.65	7.72	0.343	0.341	6.87	6.90
3.14	15.6	0.201	0.204	0.042	0.042
2.37	88.4	0.027	0.026	2.10	2.16
2.49	161.0	0.015	0.015	1.14	1.14
2.45	205.0	0.012	0.011	0.907	0.903

* Calculated.

† Determined as calcium picrolonate.

culated by dividing the amount of Ca(e) by the ratio $Ca^{45}(e)/Ca^{45}(s)$. By means of these values the specific activity of the Ca in the liquid phase can be calculated for those samples in which the Ca could not be determined chemically.

TABLE 3

Distribution of Ca and Ca^{45} between exchangeable and solution phases of bentonite systems

Ca(E)	Ca(s)	$\frac{Ca(E)}{Ca(s)}$	$\frac{Ca^{45}(E)}{Ca^{45}(s)}$	SPECIFIC ACTIVITY	
				Ca(e)	Ca(s)
mgm.	*mgm.*			$\times 10^{-5}$	$\times 10^{-5}$
9.02	0.015	601.0	31.6	1.16	1.18*
8.14	0.067†	121.0	23.8	29.2	29.3*
15.9‡	0.845	18.4	18.9	0.351	0.360*
16.6‡	1.67	9.91	10.0	1.54	1.54
8.38	8.94	0.938	0.934	13.4	13.4
16.8‡	10.4	1.59	1.62	2.05	2.09
19.2‡	98.5	0.192	0.194	0.127	0.127
18.3‡	104.0	0.176	0.177	0.147	0.147
18.0‡	138.0	0.131	0.130	0.127	0.128
18.0‡	161.0	0.111	0.112	0.124	0.124
8.35	98.8	0.085	0.085	2.20	2.17
8.10	173.0	0.047	0.047	1.32	1.37

* Calculated.

† Determined as calcium picrolonate.

‡ Approximately 1 gm. of clay.

TABLE 4

Distribution of Ca and Ca^{45} between exchangeable and solution phases of hydrous mica systems

Ca(E)	Ca(s)	$\frac{Ca(E)}{Ca(s)}$	$\frac{Ca^{45}(E)}{Ca^{45}(s)}$	SPECIFIC ACTIVITY	
				Ca(e)	Ca(s)
mgm.	*mgm.*			$\times 10^{-5}$	$\times 10^{-5}$
5.91	0.109*	54.8	19.1	36.3	36.2†
5.93	0.333	17.5	16.0	0.266	0.266†
5.30	0.475	11.1	11.4	0.378	0.379
5.29	3.22	1.65	1.58	1.85	1.84
5.33	9.47	0.562	0.567	15.5	15.4
5.85	9.50	0.616	0.618	2.21	2.21
5.20	95.7	0.054	0.055	2.40	2.35
5.49	189.0	0.029	0.029	1.23	1.23

* Determined as calcium picrolonate.

† Calculated.

The specific activities represent the ratio of the quantity of Ca^{45} to the total quantity of Ca present. These values also are shown in tables 1 to 5. The linear logarithmic relationships of all the clays are identical, and the slope is equal to unity. That the logarithmic relationships are linear and that the specific activ-

TABLE 5

Distribution of Ca and Ca^{45} between exchangeable and solution phases of beidellite systems

Ca(E)	Ca(S)	$\frac{Ca(E)}{Ca(S)}$	$\frac{Ca^{45}(E)}{Ca^{45}(S)}$	SPECIFIC ACTIVITY Ca(e)	SPECIFIC ACTIVITY Ca(s)
mgm.	*mgm.*			$\times 10^{-5}$	$\times 10^{-5}$
12.4	0.120*	102.0	83.5	21.0	21.0†
12.5	0.223*	56.7	55.5	20.7	20.7
13.0	0.262	49.7	50.0	0.461	0.459
12.2	0.311	39.1	35.4	0.267	0.268
12.1	1.34	9.00	9.00	15.7	15.7
12.1	2.77	4.48	4.42	2.31	2.28
13.3	5.87	2.28	2.31	3.80	3.85
12.1	9.56	1.26	1.26	9.62	9.62
12.0	84.2	0.142	0.142	2.30	2.31
11.8	124.0	0.095	0.095	1.46	1.45
12.1	146.0	0.082	0.083	1.34	1.34
11.8	158.0	0.075	0.075	1.37	1.37

* Determined as calcium picrolonate.

† Calculated.

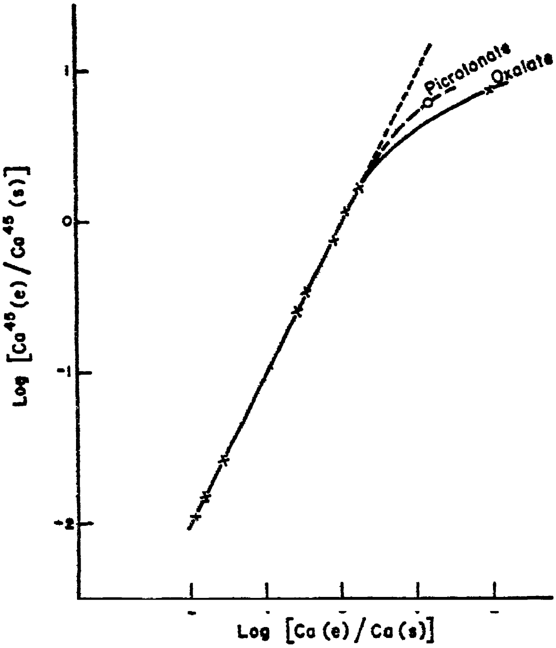

FIG. 2. RELATIONSHIP BETWEEN RATIOS OF Ca AND Ca^{45} IN HALLOYSITE

ities of the Ca in the solution and the solid phases are equal show that the Ca which is replaceable by neutral normal ammonium acetate is in equilibrium with the solution Ca.

DISCUSSION

These rate or time experiments represent an attempt to measure the rapidity of exchange of cations in clays by isotopic methods. Chemical methods employing two or more different chemical species of cations have been used frequently in this kind of study. In general, these previous studies have indicated rapid cation-exchange reactions. In many experiments the smallest time interval studied was sufficient for completion of the exchange under the conditions controlling the extent of the reaction. Gedroiz (3) found that Ca and Ba were replaced from a chernozem soil by NH_4, Na, and K when shaken for 1 minute. Hissink (4) replaced the Ca of a clay soil by Na by shaking for 3 minutes. Cernescu (2) was able to establish exchange equilibrium in "clay" in 5 minutes; permutite, however, required 10 days, and chabazite 92 days. Hissink also found that replacement of Ca from permutite by Na was much slower than from soil. Kelley (5) has suggested that exchange equilibrium is probably established more slowly in hydrous micas than in montmorillonite, because of a closer packing of the lattice layers. This is in agreement with the incomplete equilibrium shown by hydrous mica after being shaken for ½ hour. The time studies with Ca^{45} were conducted primarily to determine the minimum time for establishment of equilibrium as an essential condition for the other phases of these experiments. Rate experiments of shorter duration on dispersed clays of low electrolyte concentration would require a more specialized technique.

The finding that the solution Ca of a clay is in kinetic equilibrium with all the exchangeable Ca is not unexpected. On the basis of knowledge of exchangeable cation systems by other methods, it had been presumed that this result would be obtained. These experiments serve as direct experimental evidence of the dynamic relationship between the soluble and exchangeable fractions of a soil cation. That this kinetic equilibrium exists does not imply that all the exchangeable Ca is of the same thermodynamic activity. Marshall (9) has discussed the fact that the active Ca (and Na) of a clay possesses a wide range of activity. Clay membrane electrode measurements show that over a wide range of additions of $Ca(OH)_2$ to unsaturated clays, the activity of Ca of kaolinite increases regularly, whereas in montmorillonite relatively equivalent quantities of $Ca(OH)_2$ contribute little or nothing to the total Ca activity. In spite of this extreme difference in activity relationships of clays, the present study indicates that all of the Ca that affects such an electrode is in kinetic equilibrium. The separation of the mobile cations into solid phase and solution categories is admittedly artificial. The existence of a diffuse ion swarm, however, does not interfere with the evaluation of isotope distribution ratios when all the measured cations are in equilibrium. The isotope study has not yet been extended to soils, in which some of the nonexchangeable Ca of primary and secondary minerals also may be in kinetic equilibrium with the exchangeable and soluble fractions.

To study as simple a system as possible analytically, these experiments involved removal of all bases but Ca by preliminary treatment with calcium acetate of pH 7. It is not suggested that this eliminated exchangeable hydrogen also. It is known that clays, especially of the 1:1 lattice type, such as kaolinite and halloysite, retain exchangeable hydrogen above this pH value (10). The residual hydrogen should in no way interfere with the validity of the results, as ratios involving both the solution and exchangeable phases are used in the calculations. Although calcium acetate is most strongly buffered at a pH value considerably below 7 (12), once the clay system is brought to pH 7 by repeated treatments, maintenance of that condition during the remainder of the experiment is not difficult, as was shown by a glass electrode measurement on every replacing solution.

It is interesting to note the constancy of the exchangeable calcium for each clay. This persists over a wide variation in the amount of calcium in the solution phase, up to a range of 40,000 fold in kaolinite.

SUMMARY

By use of radioactive Ca^{45} it has been demonstrated that equilibration of Ca between the solution and solid fractions of aqueous systems of kaolinite, halloysite, hydrous mica, beidellite, and montmorillonite is complete or virtually so after shaking for ½ to 1 hour. The techniques used did not permit the study of shorter periods.

Experiments with Ca^{45} indicate that the Ca of Ca-saturated clays replaceable by ammonium acetate is in kinetic equilibrium with the soluble Ca. These results offer direct experimental confirmation of a basic premise of cation exchange that cations of an element in solution are in kinetic equilibrium with the exchangeable cations of the same element.

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FIXATION OF POTASSIUM BY CLAYS SATURATED WITH DIFFERENT CATIONS[1]

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In the study of potassium fixation by soils it is of practical as well as theoretical interest to find out to what extent cations adsorbed on the exchange complex influence the fixation of subsequently added K. Joffe and Levine showed that fixation is reduced when K has to compete with Ca for the exchange positions (7) and that the fixation increases proportionally to the amount of K entering the exchange complex (8). This was explained by the fact that K must be adsorbed before fixation can take place. From this it can be assumed that cations adsorbed or added decrease the fixation according to their replacing power or affinity for the colloid. Probably, however, competing cations will exhibit a greater influence if they are able to migrate from the adsorbed position into vacant places resulting from the release of fixed K from the interplanar surfaces of the mineral lattice. This idea is in line with Pauling's (11) and Gruner's (4) conclusions, drawn from structural analysis, that certain ions can substitute K in the mica lattice. Further, it is supported by an experiment of Barshad (1) who found that by prolonged leaching with $MgCl_2$ solution biotite could be converted into vermiculite.

If a clay is electrodialyzed or treated for a long time at high temperature with acids or salts without undue destruction of the clay minerals, some of the fixed K ions should be released. Their vacant places will then be occupied by H or by other cations from the leaching solution if proper steric conditions prevail. This process, however, does not necessarily require that the replacing ions become "fixed" in the usual meaning of this word. If K is added to such a K-depleted clay, a greater or lesser quantity of these adsorbed ions will be replaced by the K ions becoming fixed. The extent of this refixation is determined by the affinity of K for the clay compared with that of the other ions. It is very likely that ions which have a size similar to that of K and show similar chemical properties, such as NH_4, will strongly prevent this refixation. NH_4- and K-saturated clays should therefore behave in the same way upon subsequent fixation of added K. This deduction is supported by the fact that a considerable fixation of NH_4 in soils was demonstrated by Chaminade (2) and later by Joffe and

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[2] Swedish American Foundation Fellow and A. J. Roman Fellow from the Royal Agricultural College, Uppsala, Sweden. The writer is indebted to John E. Gieseking of the department of agronomy for providing the necessary facilities and to the department of chemistry, University of Illinois, for certain equipment used in this investigation. The radioactive potassium was obtained from the Clinton Laboratories, Oak Ridge, Tennessee.

Levine (6) and particularly by the studies of Stanford and Pierre (12). If the clay colloids have weak acidic properties, even H is likely to show the same effect unless the colloids are neutralized by bases, which reduces the competition of H for the exchange positions and increases the exchange capacity, thereby increasing the concentration of adsorbed K. Consequently, the K fixation should quantitatively be very much influenced by the pH at which it is induced. On the other hand, such ions as Ca and particularly Na and Mg should facilitate the fixation because they have a smaller diameter than K and in many respects different chemical properties.

So far as the author knows, no experiments have been reported dealing with the fixation of K as affected by a previous thorough saturation of the clay with different cations as discussed above. The purpose of the present investigation was, therefore, to focus attention on the problems outlined here. By use of radioactive K it was possible to study the fixation of added K on a clay saturated with H, Na, K, NH_4, or Ca as well as to obtain some insight into the mechanism of the process. Since it was found from the data thus gained that some additional information was desirable, further experiments dealing with the fixation of nonradioactive K in biotite saturated with H, NH_4, Mg, or Ba were later carried out.

EXPERIMENTS WITH RADIOACTIVE POTASSIUM[3]

Materials and methods

The experiments were carried out with Clarence soil from Illinois, classified as an illite and with an exchange capacity of 26 me./100 gm. A fraction free from organic matter and with particles <0.001 mm. was used for the experiments. Sixteen portions of 3.72 gm. (= an exchange capacity of 1 me.) were treated with 0.2 *N* HCl, *N* KCl, *N* NH_4Cl, *N* NaCl, and *N* $CaCl_2$ respectively on a sand bath at 65–70° C. for 21 days. The solutions were changed every day during the first half of the treatment and then every 2 days. Finally the colloids were washed free from acid and salts with distilled water. By this long treatment at high temperature, part of the fixed K ions were supposed to have gone into solution and their vacant places to be occupied by the displacing cations.

In one set of eight samples saturated with H, Na, NH_4, K, or Ca, the easily exchangeable ions were replaced at room temperature by adding 6 me. of $(C_2H_5)_4NI$[4], centrifuging, adding a further 3 me. of the iodide, and then washing free from the excess with distilled water. The $(C_2H_5)_4N$ ion was chosen for the replacement because it is somewhat larger than the other cations used (table 1). For this reason, it is able to replace only the easily accessible and exchangeable ions, that is, those on the outer surfaces of the mica particles, but it is not likely to replace the K fixed between the lattice sheets or the H, NH_4, Na, or Ca that has taken the place of the fixed K released from the samples treated with these ions. Thus, these eight samples were saturated with two kinds of ions, namely, $(C_2H_5)_4N^+$ in easily exchangeable position and H, K, NH_4, Na, or Ca mainly in difficultly exchangeable position. Each of the other set of eight samples was saturated with only one kind of ion, H, K, NH_4, Na, or Ca.

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[3] This part of the investigation was carried out in 1948 at the University of Illinois Agricultural Experiment Station.

[4] Obtained by the courtesy of H. A. Laitinen of the department of chemistry.

To each of the samples was added 1.5 me. of KCl mixed with an appropriate amount of radioactive K_2CO_3. The radioactive K was isotope 42 with a half-life of 12.4 hours. Where the effect of the H-ion concentration on fixation was studied, part of the K was applied as KOH or K_2CO_3 or both, according to table 2. Because of difficulties in measuring the pH of the equilibrium solutions, only the relative order of acidity is given.

Fixation was induced by heating the flasks in a water bath at 87° C. for 14 hours under conditions preventing loss of water. In the centrifuge, the exchangeable K was replaced at room temperature with 4 × 50 ml. of 0.5 *N* $BaCl_2$, followed by washing with water and treatment with 50 ml. of 0.1 *N* HCl to displace adsorbed Ba. The clays, freed from HCl, were dispersed with NaOH by vigorous shaking. In the diluted clay suspension the activity of radioactive K was determined in an annular ring type of vessel surrounding a vertical Geiger-Müller tube and compared with standards.

TABLE 1

Ionic diameters

According to Goldschmidt and Pauling

	Mg^{++}	Na^+	Ca^{++}	K^+	NH_4^+	Ba^{++}	$(C_2H_5)_4N^+$
	A.	*A.*	*A.*	*A.*	*A.*	*A.*	*A.*
Goldschmidt	1.56	1.96	2.12	2.66	2.86	2.86	4.7*
Pauling	1.30	1.90	1.98	2.66	—	2.70	—

* Not taken from Goldschmidt but approximately computed from the iodide.

Results and discussion

Table 2 shows that the effect of the various cations on the fixation of K varied greatly. Although the long treatment with H, K, and NH_4 resulted in very low fixation, the treatment with Ca and, especially, Na resulted in greatly increased fixation in accordance with the theory. It should be pointed out that this occurred even though no drying was involved. Because of high salt concentration and high temperature, which increased the thermal motion of the firmly bound or fixed K ions, these could be displaced by Ca and Na. But when the excess salts were washed away and K was added, the adsorbed Ca and Na were easily replaced and refixation of K could take place. The fact that the fixation was very low and only slightly higher in the NH_4- than in the K-saturated samples (cf. No. 7 with 11 and 9 with 12) indicates that in the fixed condition both ions are bound very firmly and with about the same strength and that they are fixed by the same mechanism. The very low value in the H-saturated samples is surprising. The clay may have lost part of its fixing capacity during the HCl treatment, or fixation may be low in a fully H (+Al)-saturated clay, an assumption which seems to be justified by the results from the following experiments.

The effect of increasing pH is in agreement with the theory and with the results obtained by Stanford (13). Because of the neutralizing effect of OH, the

TABLE 2

Fixation of radioactive K by clay from Clarence soil saturated with H^+, K^+, NH_4^+, Ca^{++}, Na^+, *or* $(C_2H_5)_4N^+$ *in exchangeable form*

3.72 gm. of clay (= 1 me. exchange capacity)

	TREATMENT PRIOR TO FIXATION															
	0.2 *N* HCl						*N* KCl				*N* NH_4Cl		*N* $CaCl_2$		*N* NaCl	
Exchangeable ions	H^+	H^+	H^+	$(C_2H_5)_4N^+$	$(C_2H_5)_4N^+$	$(C_2H_5)_4N^+$	K^+	K^+	$(C_2H_5)_4N^+$	$(C_2H_5)_4N^+$	NH_4^+	$(C_2H_5)_4N^+$	Ca^{++}	$(C_2H_5)_4N^+$	Na^+	$(C_2H_5)_4N^+$
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
pH at fixation	low	neutral	high	low	neutral	high	neutral	high	neutral	high	neutral	neutral	neutral	neutral	neutral	neutral
K_2CO_3 added ... *me.*	1	1	1	—	—	—	—	—	—	—	—	—	—	—	—	—
KOH added ... *me.*	—	—	0.5	—	—	0.5	—	0.5	—	0.5	—	—	—	—	—	—
KCl added ... *me.*	0.5	0.5	—	1.5	1.5	1	1.5	1	1.5	1	1.5	1.5	1.5	1.5	1.5	1.5
HCl added ... *me.*	1	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—
K fixed per 100 gm. clay ... *me.*	0.11	0.42	0.54	0.088	0.14	0.44	0.32	0.45	0.37	0.68	0.38	0.45	5.03	4.25	9.40	6.96
K fixed, percentage of added ...	0.27	1.05	1.35	0.22	0.34	1.09	0.79	1.11	0.92	1.69	0.94	1.11	12.5	10.5	23.3	17.3
Relative fixation, sample 4 = 1 ...	1.2	4.9	6.2	1.0	1.6	5.0	3.6	5.1	4.2	7.8	4.3	5.1	57.3	48.4	106.8	79.1

amount of adsorbed K became greater. The increase in pH resulted in an increment of 500 per cent from samples 1 to 3 and from samples 4 to 6. The fixation and the absolute increment were only a little lower in the series where the exchangeable ion consisted of $(C_2H_5)_4N^+$ instead of H^+. This fact indicates that the major part of the fixation took place by the release of difficultly replaceable H occupying the places where K has a tendency to become fixed, that is, between the lattice sheets. It is interesting to note that even in the K series the increase in pH brought about a greater fixation. An additional amount of K could probably be fixed by replacing H not previously released despite the long treatment with KCl.

It is noteworthy that the adsorbed $(C_2H_5)_4N^+$ caused a decrease in the fixation in the H-, Na-, and Ca-treated samples but an increase in the K- and NH_4-treated ones. This might, at first sight, seem inconsistent, but it can be easily explained. $(C_2H_5)N^+$ is more firmly adsorbed by the clay than are H^+, Na^+, and Ca^{++}, which leads to a reduced adsorption of the added K^+ and hence a lower fixation in the former case than in the latter. In the K series, the added radioactive K has to compete with the inactive K for the fixation positions in the K-saturated sample, but this is not true to the same extent in the $(C_2H_5)_4N$-treated sample. In other words, the proportion of radioactive K is lower in the first case than in the second, and the transfer of radioactive K from exchangeable to fixed condition must therefore become less. The same explanation is valid for the NH_4 series because NH_4 shows about the same fixation tendency as K.

The slight fixation of radioactive K by the K-treated samples clearly shows that the transfer of fixed K to replaceable K was very low despite the high temperature and the long reaction time. It must be presumed that no real equilibrium exists in the fixation process until the radioactive and the inactive K are equally distributed between the fixed and the unfixed conditions. The low rate of this exchange is shown by the following simple calculations: If the fixation in sample 15 is arbitrarily considered as the maximum possible under the conditions obtaining and is put equal to the amount of K fixed during the KCl treatment and not replaced by the $(C_2H_5)_4NI$, the fixation in sample 7 is only 5.6 per cent and, in sample 9, 4.9 per cent of that considered possible. This result is in complete agreement with the slow mobilizaton of fixed K under natural conditions found by several investigators.

Several authors (3, 5, 9) have demonstrated that liming increases the fixation of K. In view of the present results this fact can be explained partly by the increase in pH and partly by the replacement of adsorbed Ca by K. If a soil is rich in lime, the adsorbed ions consist mainly of Ca, which is therefore likely, to some extent, to occupy places where K has a tendency to become fixed. This will be reflected in a tendency toward greater fixation of K applied in fertilizers.

EXPERIMENTS WITH NONRADIOACTIVE POTASSIUM[5]

To determine whether a similar relationship between the nature of the adsorbed ions and the capacity of K fixation to that found on the Clarence clay will appear on other materials, some further experiments were carried out using the mineral biotite.

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[5] This part of the investigation was carried out at the Institute of Pedology of the Agricultural College, Uppsala, Sweden.

The fact that the degree of K fixation was about the same on the K- and the NH_4-saturated materials may be explained by a similarity either in the ionic size or in the chemical and physical properties of the K and NH_4 ions or by both factors together. So far as the ionic volume is concerned, the ions NH_4^+ and Ba^{++} have the same radius, which is about the same as that of K^+, whereas the radius of Mg^{++} is considerably smaller (table 1). If the ionic size were the only important factor, NH_4^+ and Ba^{++} should affect the K fixation in the same manner, whereas Mg^{++} should behave differently and increase the fixation, in accordance with the results obtained on the Na- and Ca-saturated Clarence soil.

In the following experiments, the fixation of K in biotite previously saturated with H, NH_4, Mg, and Ba respectively was studied. The experiments also included a comparison between the fixation in biotite pretreated with 0.2 *N* HCl and in biotite pretreated with 0.02 *N* acetic acid, to obtain information of whether the low K fixation in material H-saturated by HCl treatment is caused by a destruction of the silicates or is due to the H(+Al)-saturated condition. Biotite is particularly well suited for this purpose, since it is known as a rapidly weathering material.

Experimental

The biotite used in the experiments was ground and sifted through a 0.2-mm.-mesh screen. It was H-saturated by daytime treatment on a steam bath for 21 days with (*a*) 0.2 *N* HCl and (*b*) 0.02 *N* acetic acid in large quantities. NH_4-, Mg-, and Ba-saturated biotites were obtained as in the previous experiments. After the excess electrolytes had been washed away by centrifuging, an amount of KCl corresponding to 13 me. per 100 gm. of biotite was added, the pH in the H-biotite being regulated by the substitution of KOH for KCl. Fixation was induced by heating on a steam bath for 9 hours. The amount of fixed K was obtained as the difference between the K added and that recovered by one shaking with neutral normal ammonium acetate followed by an ample leaching on filter paper with the same solution.

Results and discussion

From table 3 it is evident that fixation increases materially with decreasing H-ion concentration. This is in agreement with the previous results.

It appears further that the degree of K fixation was about the same in the biotite treated with 0.2 *N* HCl as in the one treated with 0.02 *N* acetic acid. Since it is highly probable that in the latter case the acid (pH = 3.2) exerted only a slight dissolving effect on the mineral—no ocular change appeared—whereas the HCl caused a perceptible decomposition of the biotite and a noticeable increase in its volume, the remarkably low fixation in H-saturated materials can be assumed to depend on the H(+Al)-saturated condition, caused even by very weak acids, rather than on destruction of the lattice by the acid treatment.

As might be expected, the fixation in the NH_4-saturated mineral was very low (table 3). Surprisingly high, however, was the fixation in the Mg- and Ba-saturated biotites, where it amounted to 91 and 76 per cent of the added K respeltively.

In view of the essential difference in ion volume and chemical properties of Mg and K, it is conceivable that the Mg ions that have occupied places where K has a tendency to become fixed are easily replaced by the subsequently added K ions.

The noteworthy fact that fixation in the Ba-biotite was 50 times as great as that in the NH_4-biotite, despite the equal volume of Ba^{++} and NH_4^+, clearly shows that properties other than the ion volume also play a very important role in the fixation tendency of the ion and in the capacity of the ion in adsorbed position to prevent fixation of another ion. Furthermore, it indicates that, at least for micaceous material, no such intimate relationship between ionic volume and tendency toward fixation exists as that concluded by Page and Baver (10) for expanding minerals.

TABLE 3

Fixation of K by ground biotite saturated by long treatment with H^+, NH_4^+, Mg^{++}, or Ba^{++}

	TREATMENT PRIOR TO FIXATION								
	0.02 *N* CH_3COOH			0.2 *N* HCl			*N* NH_4Cl	*N* $MgCl_2$	*N* $BaCl_2$
Biotite.........*gm.*	30	30	30	30	30	30	15	15	15
KCl added......*me.*	4	2	0	4	2	0	2	2	2
KOH added.....*me.*	0	2	4	0	2	4	—	—	—
pH at fixation......	low	medium	high	low	medium	high	neutral	neutral	neutral
K fixed per 100 gm. biotite........*me.*	0.18	0.52	0.74	0	0.71	0.87	0.20	11.89	9.86
K fixed, percentage of added..........	1.38	3.96	5.65	0	5.44	6.69	1.53	91.2	75.6
Relative fixation...	1.0	2.9	4.1	0	3.9	4.8	1.1	66.1	54.8

SUMMARY AND CONCLUSIONS

A micaceous clay treated for 21 days at a temperature of 65–70°C. with HCl, NaCl, KCl, NH_4Cl, and $CaCl_2$ respectively was used for the study of the influence of adsorbed cations on the fixation of subsequently added radioactive K. By this long treatment, fixed K was replaced and the clay became highly saturated with the other cations. The fixation was found to be very low when the clay was saturated with H, K, or NH_4 but very high when saturated with Ca and, especially, with Na. The results were similar when the readily exchangeable H, Na, K, NH_4, and Ca were replaced by $(C_2H_5)_4NI$ prior to fixation, which indicates that those ions had occupied vacant places resulting from the release of fixed K.

Fixation experiments with ordinary K were also carried out on ground biotite saturated in a similar way with H, NH_4, Mg, and Ba. The fixation values were very low for the H- and NH_4-biotite but very high for the Mg-saturated biotite and even for the biotite saturated with Ba, which is surprising, since Ba^{++} and NH_4^+ have the same volume.

The experiments can be said to have demonstrated the intimate relationship between the nature of the adsorbed ions and the degree of fixation of subsequently added K. Naturally, the experimental values mean only the amount of fixation under the given conditions and give neither the total fixation capacity of the materials nor the rate of fixation.

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METHOD FOR DETERMINING RELATIVE PHOSPHATE-FIXING CAPACITY OF ACID SOILS[1]

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Phosphate fixation by acid soils has been the subject for research by many investigators, and various theories relative to the mechanism of such fixation have been evolved. It has been widely accepted that chemical precipitation of soluble phosphates by iron and aluminum accounts for much of the phosphate fixation in acid soils (2, 5, 6, 7, 10, 14, 15, 36, 41, 42). Other investigators (1, 4, 8, 19, 21, 28, 29, 30, 31, 33, 38, 43) have concluded that anion-exchange surfaces of clay minerals are effective in the removal of soluble phosphate from the soil solution. These investigators generally agree that the exposed iron and aluminum atoms of the crystal lattice of the clay minerals are responsible for the activity of the clay in the phosphate-fixation process. Perkins *et al.* (25), Black and Low (1, 22), and Sieling (36) have shown that kaolin, unless finely ground or subjected to chemical treatment that will break down its structure to give free alumina, possesses little capacity to fix phosphate.

From all of these researches it becomes apparent that iron and aluminum are the principal agents responsible for phosphate precipitation in acid soils. Gaarder (10) and Karlson and Mattson (18) have shown that phosphate is adsorbed by many soil particle surfaces in a loosely fixed or "saloid-bound" form. They consider that this "saloid-bound" phosphate is available for plant use and that it is readily replaced from the adsorbed state by neutral salt solutions which would not be effective in replacing the chemically bound or fixed phosphates.

Most methods for determining the phosphate-fixing capacity of soils and soil separates are based on treatment of a sample with a solution of known phosphate concentration under specific conditions (3, 8, 12, 24, 26, 27, 32). This is followed by a separation of the sample from the saturating solution by filtration or centrifugation and washing of the residual phosphated sample with an appropriate solvent to remove the excess reagent used for saturation. The phosphated sample is then treated with a reagent to displace the fixed phosphate, which is subsequently determined by a recognized method. Many difficulties are encountered when this procedure is used. It is very difficult to remove the excess reagent with the selective solvent without a loss of phosphate from hydrolysis. The displacement of the fixed phosphate by most of the reagents employed results in the solution of organic phosphates with resulting high values for phosphate fixation. Soils treated with strong phosphates become dispersed, making filtration procedures very difficult. This difficulty may be resolved by centrifugation technique, which requires considerable time to complete the saturation of the sample with the reagent, removal of the excess reagent, and removal of the fixed phosphate from the soil for determination: about nine or ten centrifugings are required for each sample.

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If iron and aluminum are the principal substances that react with phosphate to give relative values for phosphate fixation in these direct methods, it seemed logical that these active fixing components might be extracted and determined directly to give a relative value for fixing capacity of a soil which would correspond to that obtained by the more laborious direct method. The objective of this research was to develop an indirect method for determining the relative phosphate-fixing capacity of acid soils based on the extraction of the iron and aluminum from the soil under controlled conditions and the subsequent determination of these elements together in the extract.

EXPERIMENTAL

Determination of iron and aluminum together in solution

Before a satisfactory method, based on the amount of extractable iron and aluminum, for estimating phosphate-fixing capacity could be developed, it was necessary to find a simple but accurate method for determining these elements together, with special reference to their combining power for phosphate or their chemical equivalency. Any gravimetric method involving direct weighing of iron and aluminum precipitates would prove unsatisfactory, as no indication of the combining power would be obtained, unless the elements were first separated quantitatively, because of the difference in their equivalent weights.

Several methods were investigated including that of Kampf (17), which allows for determining iron and aluminum together by precipitating both with 8-hydroxyquinoline, dissolving the precipitate, and subsequently brominating the equivalent 8-hydroxyquinoline with standard bromide-bromate solution. The literature offers a number of means by which iron and aluminum can be separated and appropriate methods for determining each separately. Of these, the authors used that given by Smith (37) for the separation and determination of iron with cupferron, and the method of Kolthoff and Sandell (20) for the determination of aluminum with 8-hydroxyquinoline.

Although these methods are satisfactory, the desirable accuracy was not obtained with the Kampf method because of difficulties encountered in obtaining a satisfactory end point in the titration, and the separation of the elements in the Smith procedure required considerable time. It was believed that a method might be developed whereby iron and aluminum could be determined in solution together using phosphate as the precipitating agent. The phosphate combined could then be determined by any appropriate method and would not only give the combining or fixation power of both the iron and aluminum, but would also give this value in terms of phosphate.

Scott (34) gives a method of determining aluminum as the phosphate in which the pH of the solution is adjusted by using methyl orange as an indicator and the aluminum is precipitated with phosphate, washed with hot 5 per cent ammonium nitrate, and finally ignited to $AlPO_4$. Swenson, Cole, and Sieling (40) showed that aluminum and iron undergo the same general reactions in the presence of phosphate; the maximum precipitation of basic iron phosphate was at pH 2.5 to 3.5, and of basic aluminum phosphate at pH 3.5 to 4.0. These investigators showed that under the proper conditions of pH and phosphate concentration either iron or aluminum was precipitated stoichiometrically by phosphate—1 mole of iron or aluminum precipitated 1 mole of phosphate to form compounds of the same general formula. An attempt was made, therefore, to determine iron and aluminum together in solution as total sesquioxides, without regard to the relative amounts of either present, by using phosphate as the precipitating reagent and by controlling the pH and other factors affecting the reaction. It was necessary that the determination give a value representing the combining power of the total sesquioxides and not a weight value, as the relative proportions of iron and aluminum in a soil extract may vary widely from one soil to another, and both are almost invariably present. The detailed method developed follows:

> A solution free of organic matter and containing between 0.05 and 1.0 millimol of iron and aluminum or either element separately is placed in a 250-ml. beaker and 100 ml. of 0.03 *M* KH_2PO_4 (3 millimols), 10 ml. of 20 per cent NaCl, and 3 ml. of 60 per cent $HClO_4$ are added. Two drops of methyl orange is then added and the solution is heated to boiling and titrated with approximately *N* NaOH until a color change to yellow is observed. Dilute HCl is used to back-titrate the solution to a slight orange color. This is the color change interval of methyl orange and is at a pH of approximately 3.4–3.5. The sample is then heated near the boiling point on the hot plate for 30 minutes. After digestion, the hot solution is filtered through No. 42 Whatman filter paper and the filtrate discarded. The precipitation beaker is washed thoroughly with hot 1 per cent NaCl adjusted to pH 3.4 and the wash liquid poured over the precipitate on the filter. This washing is allowed to drain completely from the filter, and the filter and precipitate are washed two additional times with the hot 1 per cent NaCl solution. Care should be taken that the precipitate is disturbed as little as possible by directing the wash solution around the top of the filter. When the third washing has completely drained through the filter, hot 1 per cent perchloric acid is used to dissolve the precipitate on the filter into a 500-ml. volumetric flask. *The precipitate must not be allowed to dry.* The precipitation beaker is washed thoroughly with the hot perchloric acid solution and the contents are poured through the filter. After cooling, the solution is made to volume. After appropriate dilution, an aliquot is taken for the determination of phosphate by the method of Sherman (35).

The upper limit of 1 millimol of the iron and aluminum should not be exceeded, or difficulty in removing the excess phosphate, especially that which is "saloid-bound," will be encountered. The sodium chloride and the perchloric acid added prior to precipitation and the sodium chloride solution used for washing the precipitate are necessary to prevent the saloid binding of phosphate, to aid in removal of the excess phosphate, and to prevent peptization of the insoluble basic iron and aluminum phosphates. Other salts such as NH_4NO_3, KNO_3, and KCl could be used as well for this purpose. The precipitation is carried out at pH 3.4–3.5, which is within the range of maximum precipitation of both iron and aluminum as shown by Swenson *et al.* (40). The sodium chloride wash solution was adjusted to the same pH to prevent solution of the precipitates during removal of the excess phosphate. Experience showed that a very fine, highly retentive filter paper was essential to prevent loss of the basic aluminum phosphate which precipitates in a very fine state under the conditions of the determination. Excessive washing of the precipitate should be avoided.

The reliability of this method for determining either the iron or the aluminum or both together in a solution is indicated in table 1. Stock solutions of iron and aluminum chlorides were used to prepare samples 1, 2, and 3. Samples M_2, M_3, and M_4 were soil extracts obtained later in this investigation. In all cases the individual iron determinations were made by the cupferron method of Smith (37), and the aluminum by the 8-hydroxyquinoline method of Kolthoff and Sandell (20) after removal of the iron by cupferron.

This method is accurate for the determination of iron and aluminum together in solution and can be used for determination of these elements in soil extracts, clays, cement, and other materials where total quantities of sesquioxides are desired without reference to the individual elements.

TABLE 1

Determination of iron and aluminum by coprecipitation as basic phosphates at pH 3.4 and by separate determination of iron with cupferron and aluminum with 8-hydroxyquinoline

SAMPLE	ADDED		IRON DETERMINED BY CUPFERRON	ALUMINUM DETERMINED BY 8-HYDROXYQUINOLINE	TOTAL OF IRON AND ALUMINUM	IRON PLUS ALUMINUM FOUND BY CO-PRECIPITATION WITH PHOSPHATE AT pH 3.4
	Fe	Al				
	mmol.	*mmol.*	*mmol.*	*mmol.*	*mmol.*	*mmol.*
1	—	1.00	—	1.016	1.016	0.990
2	1.00	—	1.001	—	1.001	0.995
3	0.50	0.50	0.503	0.508	1.011	0.996
M_2	—	—	24.25	13.40	37.6	37.3
M_3	—	—	20.25	16.29	36.5	35.8
M_4	—	—	13.02	21.75	34.8	34.3

Developing the method for extracting iron and aluminum from soils

Citric acid and citrates have been shown to be effective in dissolving fixed phosphates from soils (8, 9, 16). Swenson *et al.* (40) have reported that citrates, when present in sufficient quantity, have the ability to prevent precipitation of iron or aluminum as phosphates or hydrates. Recent observations by Struthers and Sieling (39), in this laboratory, have shown that 1 millimol of citrate will almost completely complex 1 millimol of iron and prevent precipitation by either phosphate or hydroxide at pH 4.0 to pH 6.0. Only 0.5 millimol of citrate was required to complex 1 millimol of aluminum under the same conditions. Thus citrate has the property of dissolving both iron and aluminum even when these elements have been precipitated by phosphate or hydroxyl because of the great stability of the complex ions formed. Citric acid was chosen as the solvent for the iron and aluminum in soils because of this ability to dissolve relatively insoluble compounds of iron and aluminum which would be effective in precipitating phosphate in the direct method or under natural conditions in the soil and because it could be easily removed from the extract by oxidation and thus not interfere with the subsequent quantitative determination of these elements. The concentration of the citric acid solution used and the time of extraction of the soil with the solution were determined by systematically studying the effects of these variable factors on the amount of iron and aluminum extracted.

Influence of concentration of citric acid on amount of iron and aluminum extracted from soils. A series of samples of a soil were digested for 1 hour in a boiling water bath with citric acid, filtered while hot, and washed thoroughly with hot water, and the content of iron and aluminum was determined in the filtrate. Each set of duplicate samples was treated with a varying molar concentration of citric acid ranging from 0.1 to 1.0 inclusive, but otherwise they received the same treatment. The amounts of iron and aluminum extracted, expressed as phosphate-fixing capacity per 100 gm. of soil, as influenced by the molarity of the citric acid are shown graphically in figure 1.

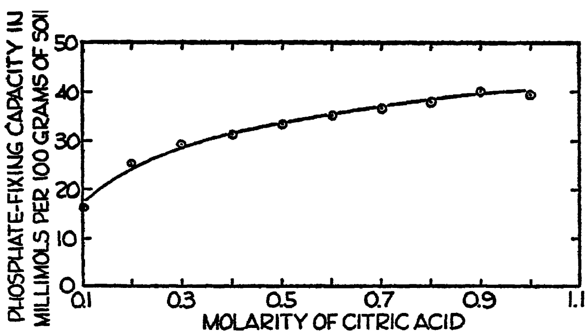

FIG. 1. EFFECT OF CONCENTRATION OF CITRIC ACID ON AMOUNT OF IRON AND ALUMINUM EXTRACTED FROM A SOIL

A gradual increase in iron and aluminum extracted as measured by the phosphate-fixing capacity can be seen. Black (1) found that increasing the concentration of phosphate in the saturating solution increased the phosphate-fixing values obtained. Similar observations were made by Ghani and Islan (11). Rubins and Dean (31) used several extracting solutions including phosphate, arsenate, fluoride, and hydroxyl in their studies of anion exchange, and found that in every instance increasing the concentration of the extracting solution increased the anion-exchange capacity values obtained. Low and Black (22) showed that with increased concentration of phosphate solution a corresponding increase in phosphate-fixing capacity of the kaolin substrate occurs. They offered the explanation that kaolinite dissociates weakly into alumina and silicate ions, and in the presence of a substance which forms a stable complex with either the alumina or the silicate, a continuous breakdown of the kaolin molecule occurs. It is thus apparent that a concentration of extracting solution which will give an absolute value of phosphate-fixing capacity cannot be found, since the value will increase progressively with an increase in concentration as a result of continuous release of aluminum or iron by the breakdown of the clay mineral.

Influence of time of digestion on phosphate fixing values. Several investigators (8, 21, 22, 25, 36) have reported that phosphate-fixation values increased progressively as the time of treatment of the soil with the reagents was increased. Different reagents produced different rates of increase in these values, depending upon their relative effectiveness in breaking down the soil minerals. To determine the exact time of digestion required to give values for phosphate fixation of soils by the citric-acid–extraction method which would be comparable to those obtained by the direct phosphation method, it was essential to determine the influence of time of digestion on values obtained by both of these methods.

In a boiling-water bath, 25-gm. samples of five soils representing varying phosphate-fixing capacities were digested with 75 ml. of 0.5 *M* citric acid in flasks attached to reflux condensers for periods ranging from 1 hour to 4 weeks. The digested soils were filtered while hot and were washed with hot water. Iron and aluminum extracted in different periods of time, expressed in terms of millimols of phosphate-fixing capacity, are shown in table 2.

TABLE 2

Influence of time upon phosphate-fixing capacity of soils measured by the citric acid method and by the method of Piper

Capacity in millimols per 100 gm. soil

TIME	PHOSPHATE-FIXING CAPACITY									
	Citric-Acid Method					Piper's Phosphate Method				
	Soil 718A	Soil 2	Soil 3	Soil 5	Soil 6	Soil 718A	Soil 2	Soil 3	Soil 5	Soil 6
hours										
1	20.6	8.8	29.6	24.1	56.6	14.1	4.5	20.3	17.1	30.5
2	24.6	12.1	36.1	30.5	68.4	18.5	5.4	24.5	20.0	37.1
3	29.8	14.3	41.0	35.2	76.1	20.3	6.2	26.3	23.2	45.6
4	31.8	16.0	43.0	36.7	76.8	20.9	8.0	28.6	24.0	54.1
5	32.4	17.1	43.6	38.6	80.0	22.9			35.9	56.9
168	63.3					29.4				
336	72.9					43.5				
504	73.6					44.0				
672	82.4					48.6				

The phosphate-fixing capacities of these same five soils were determined by a direct phosphation method similar to that described by Piper (27). The samples were phosphated with a solution of 0.5 *M* KH_2PO_4 adjusted to pH 3.4 with 0.5 *M* H_3PO_4. Centrifuge tubes containing the samples and phosphating solution were attached to reflux condensers and heated in a boiling-water bath for periods ranging from 1 hour to 4 weeks. After the desired period of phosphation had elapsed the phosphate fixed was determined by the modified Piper method described later. The values for phosphate-fixing capacities of the five soils as influenced by time of treatment are shown in table 2.

Obviously neither of these methods will give an absolute value for phosphate-fixing capacity, but they will give relative values which are comparable when the conditions of the determinations are fixed.

For comparable time the citric-acid method gave higher values than the Piper method. This indicates that citric acid has a greater coordinating power with iron and aluminum than does phosphate. These results substantiate the findings of many other investigators (8, 9, 13, 16, 21, 40, 43). The increase in values obtained with increase in time of digestion suggests a continuous breakdown of the clay minerals involved, with accompanying release of iron and aluminum that can participate in the precipitation of phosphate. Low and Black (22), Ghani and Islan (11), Black (1), Perkins and King (26), and Dean and Rubins (8) used phosphate, 8-hydroxyquinoline, arsenate, hydroxyl, and other materials and found phosphate-fixation values increased with increasing time of digestion.

It was observed that the values obtained by 1-hour extraction with 0.5 *M* citric acid were strikingly similar to the values obtained by 4-hour digestion with 0.5 *M* KH_2PO_4. To compare values obtained from the two methods it was decided to adopt 1-hour digestion with 0.5 *M* citric acid as standard in the citric-acid procedure and 4-hour digestion with the 0.5 *M* KH_2PO_4 adjusted to pH 3.4 with 0.5 *M* H_3PO_4 as standard for direct phosphation method of Piper.

TABLE 3

Phosphate-fixing capacity of soil 718a after extraction with citric acid for various periods

	SAMPLE							
	1	2	3	4	5	6	7	8
Time of extraction with 0.5 *M* citric acid................. *hrs.*	1	5	10	15	20	168	336	672
Phosphate-fixing capacity of soil after extraction.............. *mmol./100 gm. soil*	9.6	6.3	4.8	2.5	2.3	1.4	1.4	1.2

Reduction of phosphate-fixing capacity of soil by removal of iron and aluminum with citric acid. Eight samples of soil 718a were digested with 0.5 *M* citric acid for periods ranging from 1 hour to 4 weeks. The soils were filtered, washed with hot water, and allowed to dry for several days. These extracted soils were then tested for phosphate-fixing capacity by the direct phosphation method. The values for the residual phosphate-fixing capacity are recorded in table 3.

The results indicate that the active components of the soil responsible for phosphate fixation are soluble in citric acid and are probably iron and aluminum. Kelley and Midgley (19), Dean and Rubins (8), Coleman (5), Metzger (24), and others have presented similar findings. The fact that the soils fix phosphate after long periods of digestion with citric acid indicates that there is a continuous breakdown of soil minerals by the phosphate reagents; however, the more readily soluble iron and aluminum are almost completely removed by citric acid in 15 hours. These most readily soluble fixing components are believed to be largely responsible for phosphate fixation under field conditions.

Procedure for determinating phosphate-fixing capacity by citric acid method. It is obvious from the results just presented that there is no absolute value for phosphate-fixing capacity; however, under fixed experimental conditions a relative value which may be used for comparing soils can be obtained. The specific experimental details of the method developed in this study are as follows:

A prepared soil sample of 20 gm. is weighed into a 400-ml. beaker, mixed with 75 ml. of 0.5 *M* citric acid, and digested in a boiling water bath for 1 hour with periodic stirring. The solution is then removed and filtered through No. 41 or 40 Whatman filter into a 500-ml. volumetric flask, followed by washing with hot water. When the filtrate is sufficiently cooled, it is made to volume, mixed, and a 25-ml. aliquot pipetted into a 250-ml. beaker. The aliquot is evaporated nearly to dryness and 10 ml. of concentrated HNO_3 is added. The mixture is heated on the hot plate for about 20 minutes and 5 ml. of 60 per cent $HClO_4$ is added. Heating is continued until heavy white fumes of $HClO_4$ appear, then for an additional 20 minutes to ensure complete oxidation of all organic matter and the iron. When the sample is sufficiently cool to avoid spattering it is diluted with 20 ml. of distilled water. Further treatment is then continued in detail as described under method for the determination of iron and aluminum by precipitation as the basic phosphates, except that the 3 ml. of $HClO_4$ need not be added because it is already present in the processed soil extracts. The number of millimols of phosphate found is equivalent to the number of millimols of both iron and aluminum present in the original citric extract of the soil, and represents the fixing capacity of that soil when calculated in terms of millimols per 100 gm. of soil.

Comparison of citric acid method and Piper's method for determining phosphate-fixing capacity of representative acid soils. Since most of the current methods of determining phosphate-fixing capacity are similar to Piper's (27) tentative method for determining anion exchange, it was believed that a comparison of the values obtained from the citric-acid method and a method which was essentially that of Piper would be of some value in establishing the validity of this developed method. The Piper method was modified as follows, consistent with the observation that saloid-bound or adsorbed phosphate could be removed by a high concentration of neutral salt.

Five-gram samples of soil were weighed into 50-ml. centrifuge tubes, and enough 0.5 *M* $KH_2PO_4 \cdot H_3PO_4$ at pH 3.4 was added to bring the total volume to 40 ml. The mixture was thoroughly stirred and then digested on a boiling water bath for 4 hours. At the end of this time the centrifuge tubes were removed and centrifuged for 15 minutes at 2,500 r.p.m. The supernatant liquid was poured off and 40 ml. of hot 1 per cent NaCl added to each sample. The tubes were thoroughly shaken, heated for 30 minutes on the water bath, and then centrifuged again. The supernatant liquid was poured off and a second washing with 1 per cent NaCl made. Following this, three washings were made with 70 per cent ethyl alcohol containing 2 per cent NaCl. The samples were thoroughly shaken each time and centrifuged without being heated. All liquid was allowed to drain out of the centrifuge tubes after each centrifuging. The samples were digested on the hot water bath for 1 hour with 0.5 *M* citric acid to displace the fixed phosphate, filtered into a 250-ml. volumetric flask, cooled, and made to volume, after which a 25-ml. aliquot was taken for oxidation with HNO_3 and $HClO_4$. Oxidation was continued to dense fumes of $HClO_4$. The oxidized material was cooled and filtered into a 250-ml. flask, made to volume, and a 10-ml. aliquot taken for phosphate determination by the method of Sherman (35). The 10-ml. aliquot represented 20 mgm. of soil and was calculated on the basis of millimols of phosphate fixed per 100 gm.

Thirty-nine soils from Alabama, North Carolina, New Jersey, Maine, Vermont, and Massachusetts were used in the comparative study of these methods.

TABLE 4

Comparison of citric-acid and modified Piper methods for determining phosphate-fixing capacity of representative acid soils*

Capacity in millimols per 100 gm. soil

SOIL NO.	SERIES	LOCATION	DESDRIPTION	pH	PHOSPHATE-FIXING CAPACITY	
					Citric-Acid Method	Piper Method
A3	Norfolk loamy sand	Alabama	Low P fixing	4.6	7.7	7.3
NC2	Alamance	North Carolina	1.64 anion-exchange capacity†	4.3	7.2	7.5
854	Norfolk sandy loam (deep phase)	Alabama	A horizon, 5 inches	5.6	4.7	7.8
2	Agawam FS	Amherst, Mass.	Subsoil	5.5	8.8	8.0
A2	Cecil silty clay loam	Alabama	Medium P fixing	4.6	12.4	10.6
813	Norfolk fine sandy loam	Alabama	A horizon, 5 inches	3.9	10.6	11.5
872	Hartsells fine sandy loam	Alabama	A horizon, 5 inches	4.5	10.0	12.3
NJ1	Evesboro loamy sand	New Jersey	Fixation 8.8 me./100 gm. soil	4.3	10.9	12.6
V3	Poultney fine sandy loam	Vermont	25% P fixation‡	6.9	14.0	13.1
NC1	White Store	North Carolina	3.71 anion-exchange capacity/100 gm. soil	3.7	12.3	13.5
NC3	Cecil	North Carolina	4.42 anion exchange capacity†	5.3	12.9	15.5
NJ2	Colts Neck sandy loam	New Jersey	Fixa tion 25.0 me./ 100 gm. soil	4.3	12.9	17.5
718A	Suffield sandy loam	Amherst, Mass.	A horizon, 0–8 inches	4.9	20.6	20.3
A1	Eutaw clay	Alabama	High P fixing	4.4	20.6	20.8
855	Cecil clay loam	Lafayette, Ala.	A horizon, 5 inches, pH 6.2	5.8	20.1	21.7
5	Suffield sandy loam	Amherst, Mass.	Topsoil	6.2	24.1	24.0
814	Lufkin clay	Alabama	A horizon, 5 inches	4.5	25.0	25.7
3	Agawam fine sandy loam	Amherst, Mass.	Topsoil	5.3	29.6	28.6
735A	Becket stony loam	Tolland, Mass.	A horizon, 2–3 inches	4.0	29.8	32.0
M3	Caribou loam	Maine	Surface soil	4.1	35.8	33.7
M4	Caribou loam	Maine	Surface soil	4.6	34.3	34.2
V2	Calais loam	Vermont	57.5% P fixation‡	5.3	35.9	35.6
M2	Bangor loam	Maine	Surface soil	5.8	37.3	38.6
732B	Berkshire sandy loam	Hawley, Mass.	B horizon, 7–20 inches	4.9	41.5	39.9
M7	Caribou loam	Maine	Subsoil	5.2	38.0	40.3
V4	Suffield sandy loam	Vermont	65% P fixation‡	4.9	38.2	40.7
M6	Caribou loam	Maine	Surface soil	5.2	38.6	40.8
M1	Bangor loam	Maine	Surface soil	5.6	39.9	40.8
M5	Caribou loam	Maine	Surface soil	5.2	44.4	44.5

TABLE 4—*Continued*

SOIL NO.	SERIES	LOCATION	DESCRIPTION	pH	PHOSPHATE-FIXING CAPACITY	
					Citric-Acid Method	Piper Method
732C	Berkshire sandy loam	Hawley, Mass.	C horizon, over 20 inches	4.5	40.6	45.0
NJ3	Norton silt loam loam	New Jersey	Fixation 87.5 me./100 gm. soil	4.6	40.0	45.2
732A	Berkshire sandy loam	Hawley, Mass.	A horizon, 0–7 inches	4.6	44.6	46.0
731B	Blandford loam	Hawley, Mass.	B horizon, 8–24 inches	4.2	47.1	46.5
719A	Suffield silty loam	Amherst, Mass.	A horizon, 0–8 inches	5.2	46.6	47.5
VI	Podzol B horizon	Vermont	100% P fixation‡	4.1	52.0	51.4
M8	Buxton silt loam	Maine	Subsoil	5.6	48.2	51.6
731A	Blandford loam	Hawley, Mass.	A horizon, 0–7 inches	5.7	50.6	52.0
6	Suffield clay	Amherst, Mass.	Subsoil	7.8	56.6	56.9
735B	Becket stony loam	Tolland, Mass.	B horizon, 3–16 inches	5.8	81.4	74.2

* All soils except No. 6 were acid.

† Mehlich's Method (23).

‡ Heck's Method (13).

These soils represented wide variations in phosphate-fixing capacities, in pH, and in parent materials. The relative phosphate-fixing capacities of these soils as determined by the two methods are shown in table 4. The values obtained for each soil by the two methods are essentially the same, but the citrate-extracting method developed here is faster and more easily carried out.

SUMMARY AND CONCLUSIONS

A method was developed for determining the *relative* phosphate-fixing capacity of acid soils. The method depends upon the extraction of iron and aluminum from the soil by 0.5 *M* citric acid under fixed conditions of temperature and time. The amount of iron and aluminum extracted was found to be a measure of the *relative* phosphate-fixing capacity of the soil.

A method was developed for determining iron and aluminum together in solution by precipitation with phosphate under fixed conditions. The resulting precipitate is then dissolved and analyzed for phosphate to give the total iron and aluminum equivalent of the precipitate. The advantage of this method is its simplicity and the elimination of necessity for separation and individual determination of the two elements. This method can be employed for determining the total sesquioxides, iron and aluminum, in soil extracts, clays, cement, limestone, and other materials.

The *relative* phosphate-fixing capacity of 39 representative soils from Alabama, Maine, Massachusetts, New Jersey, North Carolina, and Vermont was determined by the developed method and by a direct phosphation method. The values obtained by both methods were practically the same for each soil. The soils used showed a range of values from 4.7 to 81.4 millimols phosphate-fixing capacity per 100 gm.

Both methods used gave only *relative* values for phosphate-fixing capacity of soils. Changes in the conditions of the determination would change the values obtained. The choice of standard conditions for the method developed here was based on preliminary investigations which showed that 1-hour digestion and extraction of a soil with citric acid gave values for phosphate-fixing capacity which were of similar magnitude to those obtained by 4-hour digestion in the direct phosphation method.

All the results obtained here indicate that there is no absolute value for phosphate-fixing capacity of a soil; that the agents responsible for phosphate fixation in acid soils are iron and aluminum; that the most active iron and aluminum can be removed from a soil by extraction with citric acid; and that the citric-acid extracted soil has very little phosphate-fixing capacity except that which results from the degrading action of the phosphate reagent on the more resistant minerals of the soil.

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EFFECT OF VARIOUS SOIL TREATMENTS FOR CORRECTING ARSENIC INJURY OF PEACH TREES

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In the Pacific Northwest, soils previously planted in apple trees have long been known to be unproductive for certain plants because of accumulation in the soil of residues from lead arsenate sprays. Vandecaveye *et al.* (8, 9), in studying the failure of alfalfa and barley to grow in such soils, demonstrated that arsenic in the soil was responsible for the toxic effects. Morris (6) compared the tolerance of various orchard cover-crop plants to arsenic toxic soils and found only the grasses to be resistant.

Reeves and Hutchins (7), in a plant disease report, were the first to describe the symptoms of arsenic injury on peach trees planted in old apple land. They concluded that the disorder was not a disease but a result of toxic materials in the soil. Blodgett (2) found similar symptoms on peach and apricot trees in Idaho, and produced the same disorder in potted plants by treatment with lead arsenate. With leaf analysis, Linder (4) showd that foliar injury in peach trees is associated with the arsenic content of the leaves. He found that symptoms of injury appeared in those trees that had accumulated arsenic in the leaves in excess of 2 ppm. on a dry-weight basis.

Arsenic injury in peach trees is first exhibited in midsummer by a brown to red coloration along the leaf margins. This is followed by similar discoloration scattered throughout the leaf between the veins. Many of the spot colorations die and soon drop out, giving the leaf a shot-hole appearance (fig. 1). In severely affected trees, defoliation in varying degrees up to 100 per cent follows discoloration and shot holing of the leaves. The injury is first exhibited on the older leaves. Young leaves at the tips of terminal growth often remain normal in appearance throughout the season, even though the rest of the tree may show severe injury. Affected trees are usually stunted; but there is a tendency for most injured trees eventually to recover from the disorder after a period of years. Yield of fruit is reduced, and in cases of severe injury the fruit is small and astringent in flavor.

Preliminary work was conducted during the period 1943 to 1945 on peach trees planted in arsenic-toxic soil. Soil amendments applied to these trees included ammonium phosphate, ammonium sulfate, zinc sulfate, iron sulfate, and normal superphosphate. The result of this exploratory work indicated that sinc sulfate and iron sulfate were promising for correcting arsenic injury as measured by visual symptoms. Superphosphate alone had no effect, whereas

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combination of the metal salts with nitrogen and with phosphorus reduced arsenic injury. The investigations herein reported were primarily concerned with the effect of combinations of nitrogen and zinc treatments for correcting arsenic injury of peach trees.

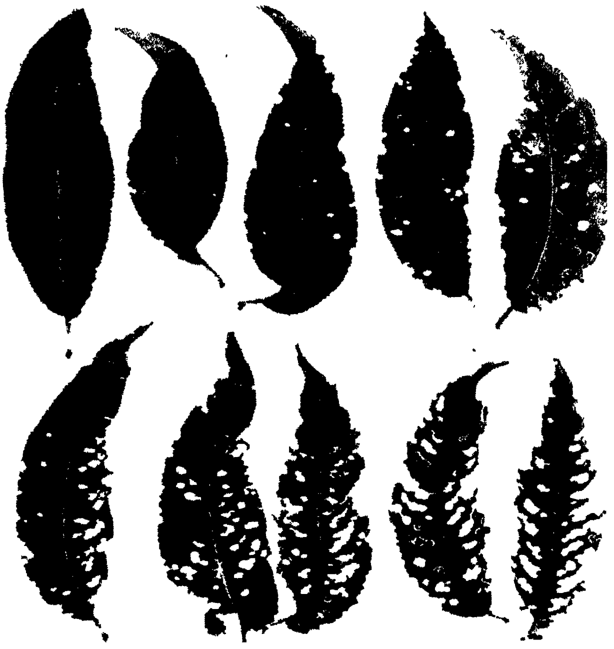

FIG. 1. ARSENIC-INJURED PEACH LEAVES FROM TREES GROWING IN ARSENIC-TOXIC SOIL; NORMAL LEAF IN UPPER LEFT

MATERIALS AND METHODS

A total of 21 experimental treatments involving 521 Elberta peach trees in six different orchards in both the Wenatchee and Yakima districts were used in this work. The trees varied in age from 3 to 6 years and were growing on land from which apples had been removed 5 to 10 years prior to the planting of peach trees. The soil reaction in the Wenatchee orchards ranged from pH 5.4 to 6.6; that of the Yakima orchards varied from pH 7.9 to 8.3. For most of the treatments applied, 10 randomized trees per treatment were used.

All soil amendment materials were broadcast around the tree in a circle approximately 8 feet in diameter. Such materials as sulfur, zinc sulfate, and ferrous sulfate were applied in one application during the dormant season; nitrogen was used in split applications, half in December or January, and half in May or early June. Both sulfate of ammonia and ammonium phosphate (16 per cent nitrogen, 20 per cent available P_2O_5) were used as a source of nitrogen. The winter applications of nitrogen were made by the grower. Whether ammonium sulfate or ammonium phosphate was used depended upon the market availability at the time. Three of the experimental orchards were irrigated by rills or ditches; in these three orchards the summer nitrogen was placed in the irrigation ditches in the immediate area of the individual trees. In the other three orchards, which were sprinkler-irrigated, the summer nitrogen was applied in a circular area about the trees as explained above. Two rates of nitrogen fertilization were used: the medium nitrogen level, or check treatment, consisted of annual applications of about 0.7 pound of nitrogen per tree, and the high nitrogen level consisted of annual applications of double that amount, or 1.4 pounds. The medium nitrogen level closely approximated the amount of nitrogen applied to peach trees annually in commercial orchards. Zinc sulfate (25.5 per cent Zn) was applied at two rates, 5 and 10 pounds per tree. Most of the zinc sulfate treatments involved but one application. Some repeat applications of zinc sulfate were made; these will be discussed later.

Records of foliage color, percentage of shot holing, and percentage of defoliation were taken at intervals during the growing season, the final ratings being made in September. At this time maximum injury from arsenic toxicity had developed, and the effectiveness of treatments could be best evaluated. Leaf samples for chemical analysis, collected in September, were washed in 4 per cent sodium hydroxide in 70 per cent alcohol and thoroughly rinsed in tap water to remove surface arsenic. After surface moisture had evaporated at room temperature, the leaves were dried in an oven at 60° C. and ground in a clean porcelain mortar. The nitrogen content of the leaves was determined by the Lindner method (5). Arsenic analyses of leaf and soil samples were made by the method of Williams and Whetstone (10), except that the chloride distillation of the A.O.A.C. method (1) was substituted for the bromide distillation. The "soluble" arsenic fraction in soils was obtained by extracting 1 part of soil with 5 parts of 0.1 *N* NaCl.

RESULTS

To establish an accurate and convenient method of evaluating the effectiveness of treatments, a comparison was made between the two most outstanding visible symptoms of injury; namely, leaf shot holing and defoliation of the tree. The relationship between shot holing and defoliation on arsenic-injured peach trees is illustrated by the regression line in figure 2, based on the ratings of 134 trees made in September 1947. The regression coefficient for shot holing on defoliation in this group of trees was +1.16 with a "*t*" value of about six times that necessary for significance at the 1 per cent point. The best time for scoring arsenic injury on peach trees is in September. By this time many of the shot-holed leaves have already abscissed. The defoliation percentage, therefore, was regarded as a more accurate and positive measure of treatments.

The effect of medium and high nitrogen and high zinc treatments in four different orchards is shown in table 1. It is apparent that high nitrogen was generally more effective in reducing defoliation than was the medium nitrogen level. When zinc was added to the treatment, defoliation was further reduced. Zinc was effective with medium nitrogen in correcting defoliation in three of the four orchards, but the combination of zinc with high nitrogen provided the best results as measured by defoliation. Thus, during the first and second years following treatments in all four orchards, trees that received zinc plus high nitrogen were significantly lower in defoliation than were the check trees (those that received the medium nitrogen treatment only). A typical tree that received the zinc plus high nitrogen is shown in figure 3, together with a typical check (medium nitrogen) tree. In 1948, the second season after treatment, defoliation was generally not so severe as in 1947 in any treatment, including the checks. The trees in the Robertson orchard are an exception; this is possibly because no winter nitrogen was applied in this orchard during the winter of 1947–48, and, therefore, the nitrogen levels for 1948 were in reality low nitrogen and medium nitrogen instead of medium and high nitrogen. With this lower nitrogen level prevailing in 1948, the check trees reverted to their former defoliation status. All other treated trees in this orchard also showed more defoliation than they did the first year after treatment. The difference required for significance indicates, however, that in 1948 the trees treated with zinc plus high nitrogen were still significantly lower in defoliation than the check trees in each of the four orchards.

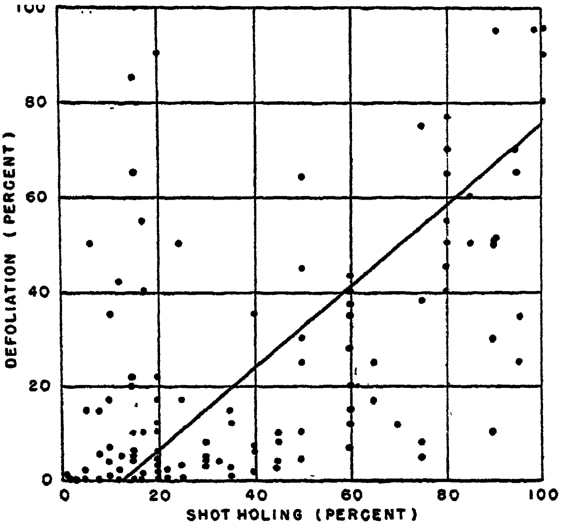

FIG. 2. DISTRIBUTION CHART AND REGRESSION LINE FOR PERCENTAGE OF SHOT HOLING ON INJURED PEACH LEAVES BASED ON THE PERCENTAGE OF DEFOLIATION OF THE TREE

Regression coefficient = +1.16; "t" = 15.9 with 132 degrees of freedom

Although there are some exceptions, treatments that provided the best correction of defoliation resulted generally in a lower accumulation of arsenic in the leaves. No measure was made of the increase in the number and size of leaves on trees receiving the applications of zinc plus nitrogen, yet observations indicated that the increase was not sufficient to account for the lower arsenic content of the leaves by mere "dilution" of a given amount of arsenic absorbed. The zinc plus nitrogen treatment resulted in a lower arsenic content of foliage in three of the four experimental orchards. Since arsenic content of peach leaves has been correlated with injury (4), the association between leaf arsenic and defoliation in the present data is of interest. The regression of leaf arsenic on defoliation, based on the trees involved in table 1 for which arsenic analyses were made, is shown in figure 4. The "*t*" value of 9.6, which is

TABLE 1

Effect of soil applications of zinc and nitrogen on peach trees growing in arsenic-toxic soil

SOIL TREATMENT*	DEFOLIATION			LEAF ANALYSES, SEPTEMBER 1947		SOIL ARSENIC, NOVEMBER 1947 0–12-INCH DEPTH		SOIL pH, 0–12-INCH DEPTH	
	Sept. 1946†	Sept. 1947	Sept. 1948	Arsenic—Shot hole leaves	Nitrogen—Normal leaves	Total	Soluble	Nov. 1946†	Nov. 1947
Johnson orchard									
	per cent	*per cent*	*per cent*	*ppm.*	*per cent*‡	*ppm.*	*ppm.*		
Medium nitrogen	73	64	16	2.75	3.20	145	1.82	5.4	6.0
High nitrogen	72	28	15	2.64	3.77	—	—	5.4	5.3
Zinc + medium nitrogen	72	26	5	—	—	—	—	5.3	5.4
Zinc + high nitrogen	71	8	5	2.05	3.63	133	1.77	5.4	5.4
Peters orchard									
Medium nitrogen	79	26	8	2.26	2.73	82	0.93	6.6	6.2
High nitrogen	80	22	3	2.46	3.22	—	—	6.6	5.6
Zinc + medium nitrogen	75	5	0	2.00	2.54	—	—	6.6	5.9
Zinc + high nitrogen	81	0	0	1.91	2.89	71	0.95	6.7	5.3
Robertson orchard									
Medium nitrogen	73	45	73	2.75	3.40	54	1.50	8.3	8.3
High nitrogen	73	17	28	1.90	3.46	—	—	8.3	7.9
Zinc + medium nitrogen	73	8	56	—	—	—	—	—	—
Zinc + high nitrogen	73	4	9	1.85	3.56	49	1.39	8.3	7.8
Nelson orchard									
Medium nitrogen	68	17	25	1.19	2.53	36	0.92	8.1	8.1
High nitrogen	72	18	14	1.47	2.38	—	—	8.1	8.0
Zinc + medium nitrogen	72	21	22	—	—	—	—	—	—
Zinc + high nitrogen	66	2	3	1.22	2.80	30	0.51	8.1	7.4
Difference required at 5 per cent point	—	8.7	6.2	0.40	0.13	9.0	0.18	—	—

* Zinc applied in winter of 1946–1947. Nitrogen applied annually. Medium nitrogen—0.7 pound per tree per year; high nitrogen—1.4 pound per tree per year; zinc—10 pounds zinc sulfate (25.5 per cent Zn) per tree.

† Prior to treatment.

‡ Dry-weight basis.

about four times that necessary for significance at the 1 per cent point, indicates that the regression coefficient of +.046 is highly significant. The means for the two nitrogen treatments and for the zinc plus high nitrogen treatment, reported in table 1, are plotted in figure 4. The positions of these means clearly indicate that when zinc was included in the treatment, the arsenic content of the

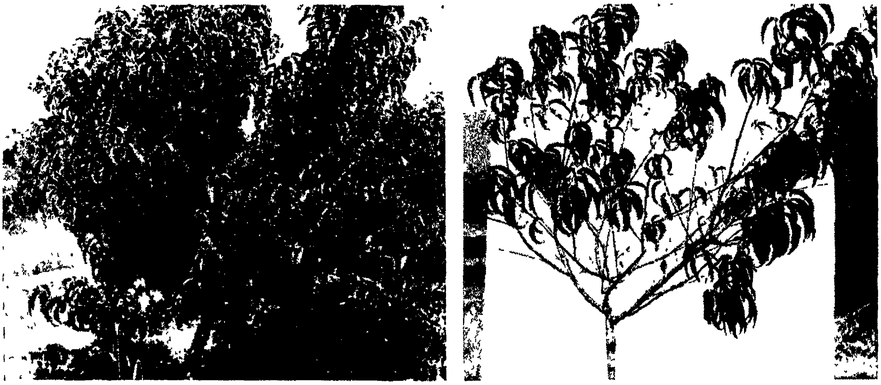

FIG. 3. TYPICAL TREES FROM ARSENIC-TOXICITY EXPERIMENTS, PHOTOGRAPHED SEPTEMBER 1947

Left, tree that received the zinc plus high nitrogen; right, medium nitrogen only (check treatment).

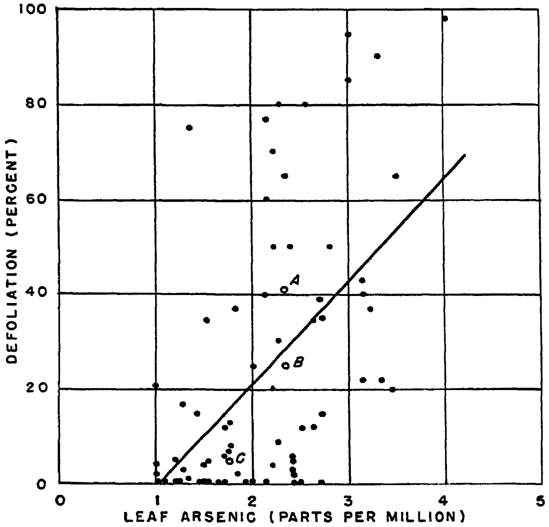

FIG. 4. DISTRIBUTION CHART AND REGRESSION LINE FOR ARSENIC CONTENT OF PEACH LEAVES BASED ON THE PERCENTAGE OF DEFOLIATION OF THE TREE

Regression coefficient = +.046; "t" = 9.6 with 72 degrees of freedom. A = mean of trees that received medium nitrogen only; B = mean of trees that received high nitrogen only; and C = mean of trees that received zinc plus high nitrogen.

leaves was lowered, although it was higher than would be expected from the regression line of all trees at a defoliation of 5 per cent (the mean defoliation of trees in the zinc plus high nitrogen treatment). This relationship suggests the possibility that the zinc plus nitrogen treatment, in addition to reducing arsenic absorption, increases the tolerance of the tree to withstand a higher level of arsenic in the leaves. Nitrogen determinations on normal leaves (table 1) indicated, as would be expected, that the high nitrogen treatments resulted generally in higher levels of nitrogen in the foliage than the medium nitrogen or check treatment.

Analyses of soil samples from the zinc plus high nitrogen treatment and the check, or medium nitrogen, treatment revealed that the total arsenic was reduced in the former treatment in all four orchards; but the reduction was significant only in the two orchards that had an initial pH on the acid side of neutrality. The reduction in orchards with soils of higher pH was consistent, but in neither case is the difference significant. "Soluble" arsenic was significantly reduced only in the Nelson orchard by the zinc plus high nitrogen treatment. In the Johnson and Robertson orchards this treatment resulted in slight reductions in soluble arsenic, but in the Peters orchard no change took place. The soil pH was not consistently affected by the medium nitrogen treatment but was generally somewhat reduced by the high nitrogen level. The addition of zinc to the high nitrogen treatment did not materially or consistently lower the pH as compared with high nitrogen alone.

Numerous other treatments were used in addition to those reported in table 1. As measured by percentage of shot holing and percentage of defoliation, the combination of medium zinc (5 pounds per tree) with high nitrogen was, in four comparisons made, about as effective in reducing injury as was the combination of high zinc (10 pounds per tree) with high nitrogen. The medium zinc plus medium nitrogen treatment proved intermediate in effectiveness between medium nitrogen (check) and either medium or high zinc plus high nitrogen. Zinc sulfate alone, used at the rate of 10 pounds per gree with no nitrogen added, reduced defoliation somewhat but was less effective than when combined with nitrogen. The effectiveness of ferrous sulfate (10 pounds per tree) was compared with zinc sulfate (10 pounds per tree) at both medium and high nitrogen levels on both acid and alkaline soils (table 2). As was found in preliminary work, ferrous sulfate was effective in correcting arsenic injury, but in less degree than zinc sulfate. A treatment consisting of 10 pounds of sulfur combined with the high nitrogen level was found to be no more effective than the high nitrogen alone on soil with a pH of 6.6; but slight reductions in arsenic injury were recorded in the three orchards where this treatment was used on alkaline soils. In two orchards (pH 8.1, 8.2) the combination of 10 pounds of sulfur plus 10 pounds of zinc sulfate with a high nitrogen level was slightly more effective in correcting injury than was the zinc plus high nitrogen treatment. A dormant spray of zinc sulfate and summer sprays of nitrogen (5 pounds of urea per 100 gallons of water), the latter being applied three times at intervals of 30 days, failed to influence arsenic injury. Analyses of leaf samples taken after the summer spray applications, however, indicated that very little nitrogen was absorbed by the foliage. Possibly, zinc absorption from the dormant application also was insufficient for effect. The injection of zinc in gelatin capsules into the trunks of trees which were maintained at a high nitrogen level resulted in intermediate correction of arsenic injury in comparison with that on check trees and trees receiving the zinc plus high nitrogen soil treatment. It is not known whether the zinc in this instance was functional in neutralizing certain "soluble" fractions of absorbed arsenic or whether it increased the tolerance of the tree for arsenic in some other manner.

TABLE 2

Comparison of soil applications of ferrous sulfate and zinc sulfate in correcting defoliation of peach trees growing in arsenic-toxic soil

SOIL TREATMENT*	DEFOLIATION		
	Sept. 1946†	Sept. 1947	Sept. 1948
Peters orchard, pH 6.6			
	per cent	*per cent*	*per cent*
Ferrous sulfate + medium nitrogen	81	28	1
Ferrous sulfate + high nitrogen	82	20	1
Zinc sulfate + medium nitrogen	75	5	0
Zinc sulfate + high nitrogen	81	0	0
Medium nitrogen (check)	79	26	8
Nelson orchard, pH 8.1			
Ferrous sulfate + medium nitrogen	73	16	22
Ferrous sulfate + high nitrogen	76	9	10
Zinc sulfate + medium nitrogen	72	21	22
Zinc sulfate + high nitrogen	66	2	3
Medium nitrogen (check)	68	17	25

* Ferrous sulfate and zinc sulfate (25.5 per cent Zn) applied in winter of 1946–1947, each at the rate of 10 pounds per tree. Nitrogen applied annually. Medium nitrogen—0.7 pound per tree per year; high nitrogen—1.4 pounds per tree per year.

† Prior to treatment.

DISCUSSION

It might be expected that soil treatments that were effective in correcting arsenic injury on peach trees would appreciably reduce the concentration of "soluble" arsenic in the soil, since "soluble" arsenic has been correlated with the effects on barley and alfalfa grown in arsenic-toxic soil (9) The reduction in "soluble" arsenic by the zinc plus high nitrogen treatment was significant, however, in only one of the four orchards (table 1). It should be pointed out that "soluble" arsenic is not necessarily a measure of *available* arsenic. Further, the potential toxicity of "soluble" arsenic would depend on the ratio of arsenite arsenic to arsenate arsenic in the soluble fraction, since the former is many times more toxic than the latter (3). It would seem, then, that the ultimate measure of treatments would be either their effect on arsenic absorption by the tree or their effect on the tolerance of the tree for arsenic, or both. In the present work, it has been shown that less arsenic was absorbed by trees treated with zinc plus high nitrogen in three out of four cases, even though the reductions in soluble arsenic in the soil by this treatment were not significant. The outstanding correction of foliar symptoms by this treatment, and the significant relationship between defoliation and arsenic content of the leaves have already been pointed out.

The correction of arsenical injury by the zinc plus high nitrogen treatment cannot be explained satisfactorily as due to lowering of the pH of the soil. As previously pointed out, soil pH resulting from this treatment was not materially different from that when high nitrogen was used alone. The lower pH resulting from addition of sulfur to the zinc plus high nitrogen treatment on alkaline soils may possibly explain why results were slightly better than when sulfur was omitted.

The duration of effect of the zinc sulfate treatment is of considerable interest commercially. Experimental evidence to date indicates that one application of zinc sulfate, together with continued high nitrogen, is sufficient to correct arsenic injury in a large measure and sustain recovery. In one orchard a repeat application of 10 pounds of zinc sulfate per tree, made 2 years after the initial zinc treatment, was found to produce only slight reduction in shot holing and defoliation in comparison with zinc-treated trees that did not receive the second application of zinc. Another group of trees, which were treated with zinc sulfate in 1945 and were maintained at a high nitrgen level for four seasons without additional zinc, showed no defoliation and an average of only 2 per cent shot holing in September 1948, or at the end of the fourth season after the zinc treatment. At this time the check trees averaged 16 per cent defoliation and 60 per cent shot holing. The check trees have shown a gradual but definite decline in shot holing and defoliation over these 4 years, which indicates that they may be recovering from the disorder. If this is the case, it is reasonable to expect that the single zinc treatment of these trees, which are now 7 years old, will be sufficient to sustain the trees permanently.

It should be emphasized that the trees involved in these investigations were 3 to 6 years old at the time of initial experimental treatment. Work is now being carried on to study the treatment of newly planted peach trees in arsenic-toxic soil.

SUMMARY

Investigations were conducted through 4 years to determine the effectiveness of various soil treatments in reducing arsenic toxicity to peach trees growing in old apple land. Under the conditions of these experiments the following conclusions are indicated:

Doubling the application of nitrogen ordinarily used on peach trees generally reduced the injury suffered from arsenic toxicity. When an application of zinc sulfate was combined with high nitrogen fertilization, however, almost complete correction was obtained in most instances.

In addition to reducing the amount of arsenic absorbed, the zinc plus high nitrogen treatment seemed to increase the tolerance of the tree so as to withstand a higher level of arsenic in the leaves.

Although ferrous sulfate was effective in correcting arsenic injury, it was not so effective as zinc sulfate.

Addition of sulfur to either the high nitorgen or the zinc plus high nitrogen treatment on alkaline soils slightly increased the effectiveness of the treatment. No difference was recorded when sulfur was added to these treatments on acid soils.

Evidence obtained thus far indicates that one application of zinc sulfate together with continued high nitrogen fertilization is sufficient to correct arsenic injury in large measure and sustain recovery of the tree.

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CRITICAL NITRATE LEVELS OF SUGAR BEETS ESTIMATED FROM ANALYSIS OF PETIOLES AND BLADES, WITH SPECIAL REFERENCE TO YIELDS AND SUCROSE CONCENTRATIONS[1]

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Interest in the application of plant analysis as a means of evaluating the nutrient status of sugar beets has increased considerably since the investigations pioneered by Gardner and Robertson (3) at Colorado, in 1935. Since then the results of several studies on technique have been reported by Ulrich (10, 11, 12, 13, 14) and by Brown (2). The early work of these laboratories centered upon the selection of the form of nutrient to be assayed and upon the plant part sampled. Preliminary results obtained here on dried plant material favored nitrate nitrogen (11) and phosphate phosphorus (12, 14) for analysis and the petiole from a recently "matured" leaf as the plant material sampled (11). Using fresh material for analysis, Brown (2) concurred with these recommendations, except that he suggested many more petioles be taken per sample than were used in our field investigations.

The technique of evaluating the nutrient status of sugar beets through chemical analysis of leaf petioles has had a number of interesting applications. One of these has been to locate areas that are likely to respond to fertilizers containing nitrogen, phosphorus, or potassium (12). Another use has been to observe the effects of fertilizers applied to beets in experimental plots (5, 14), particularly to determine whether the fertilizer applied had been absorbed by the beets and to make sure that the amounts added to the soil had been sufficient for satisfactory growth throughout the season. Still another use of plant analysis, suggested recently, is to serve as an aid to the maintenance of soil fertility through efficient fertilization and correct cultural practices. Through the systematic sampling of each crop grown on a field, the impending nutrient deficiencies can be anticipated and counteracted before a serious loss in yield and quality of crop has taken place (13).

In the use of plant analysis as a guide to fertilization of sugar beets, the

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[1] It is a pleasure to acknowledge the assistance received from many sources during the course of these experiments. Specifically, in the field experiments the California Packing Corporation provided the land and facilities for the cultural operations, collected the petiole samples, and obtained the final harvest yields; the International Minerals and Chemical Corporation furnished the fertilizers for these experiments, supported financially the chemical analysis of the petioles for nitrate nitrogen; and the research laboratory of this company at Woodland, California, supplied the data for the yields and sugar concentrations of the beets of the preharvest samples; and the Spreckels Sugar Company analyzed the beets of the pot experiment for sucrose content.

[2] Associate plant physiologist, Division of Plant Nutrition, University of California, Berkeley 4, California.

values found in a given plant part at a particular time in the field must be compared to a definite reference point, such as the critical nutrient level. Once these critical levels with their limits of variation have been established for each nutrient and for each crop, a nutritional inventory taken periodically of every crop grown on a field will aid in selecting the fertilizer program to be followed each year. At first it may be necessary to make emergency applications of fertilizers during the current growing season; but as more experience is gained, the orderly use of fertilizers would be the rule rather than the exception. It is with these objectives in view that further studies concerning the critical nutrient level have been made with beets cultured at different levels of nitrogen nutrition in pots of soil and in the field. This paper includes a study of the critical nitrogen levels that have been estimated for beets from nitrate analyses made upon blades and petioles taken from old outer leaves, from recently "matured" leaves, and from immature center leaves of plants grown in pots of soil and from recently "matured" petioles of plants grown in the field.

As the nutrient concentration of a plant or a plant part decreases, the critical concentration is that narrow range of concentrations at which growth is first retarded in comparison to plants with a higher nutrient concentration. Plants with nutrient concentrations above the critical value are well supplied with the nutrient at the time of sampling, while plants below the critical concentration are deficient in the nutrient. From this it follows that the longer in the growing season the deficiency lasts and the earlier in the growth cycle it occurs, the greater is the opportunity for increasing yields, unless other deficiencies develop immediately after correction of the first deficiency. When two or more deficiencies occur at the same time, all must be corrected simultaneously before major increases in yield take place. Predictions as to the adequacy or inadequacy of a nutrient for a crop in a given locality must be based upon evidence gained from more than a comparison of the results of a single sampling with the critical value. Only through much research can this be done effectively.

EXPERIMENTAL PROCEDURE

A uniform lot of Metz silty clay loam representing the 0–12-inch layer was taken from the vicinity of King City, California, and was placed in pots so that each contained 18 kgm. of air-dry soil.

The pots were 5-gallon galvanized-iron buckets coated on the inside with asphaltum varnish. Drainage was provided by a 3-inch hole in the bottom that was covered with an inverted china saucer. Prior to each irrigation, excess water caught in the pan below each pot was returned to the surface of the soil to minimize losses of nitrogen from the soil.

On August 19, 1948, before any water was added to the soil, a ½-inch layer of air-dry soil was removed from each pot. After thorough watering of the pot, the seed was placed upon the moist soil surface, and the dry soil was replaced. Thereafter, no water was added until the seedlings had emerged through this ½-inch surface layer of soil. In planting, the seeds were distributed in the center of each quadrant of the soil surface of the pot to ensure the presence of four plants per pot at the time of fertilization.

U. S. No. 15, whole seed, treated with Spergon, was used. As the beets grew in size, their number was gradually reduced until, on September 17, each pot had four plants in the fourth to sixth leaf stage.

On September 17, immediately after the beets were thinned, molar calcium nitrate solution was added with 1.5 liters of tap water so that each pot in the eight treatments received one of the following amounts of nitrogen: treatment 1, none; treatment 2, 0.25; treatment 3, 0.50; treatment 4, 1.00; treatments 5 through 8, 2.00 gm. On October 12, 2 gm. of nitrogen was added as before to each pot in treatments 6 through 8; and on October 18, 2 and 4 gm. to treatments 7 and 8, respectively. All treatments were replicated five times and were arranged outdoors at random within each of five blocks as required by the randomized block technique (9). Tap water, very low in salts, was added as required by the plants.

The beets were harvested from each of the 40 pots on November 5, just following a period of several days of clear and sunny weather. The plants were topped by cutting across the crown at the first leaf scar. The total weight of the tops included the crown and all the fresh and dry leaves produced by the four plants of each pot. The enlarged beet roots were washed and then dried with a cloth before they were weighed and assayed for sugar. The turgid leaves of the tops of the four beets per pot were separated according to development; namely, old outer leaves, recently "matured" leaves, and immature leaves in the center of the plant. Each category of leaves was separated into blades and petioles. The nonturgid leaves and crown were classified as residual plant material. All plant material from the tops was weighed fresh and then dried in a ventilated oven at 70 to 80° C. The total dry material produced by the tops of the four beets in each pot was obtained by summing the dry weights of all classified plant material, including the residue.

The dried plant material was ground in a Wiley mill to pass a 40-mesh sieve. Water extracts of this material were treated with hydrogen peroxide and then assayed for nitrate nitrogen by use of phenoldisulfonic acid reagent (13). Within 24 hours of harvest, the sucrose concentrations of the beets from each pot were determined on the fresh material by standard polarimetric procedures at the Spreckels Sugar Refinery at Woodland.

All experimental results were evaluated statistically by the method of analysis of variance (9). Since the growth of beets was exceptionally poor for 1.0 *N* treatment in two of the pots, designated as *A* and *B* in the graphs, these values were not included in the statistical calculations. The *F*-values recorded in table 1 were calculated by using the procedure for an unequal number of samples per treatment and combining the variation due to blocks with the error term. The block variation in the pot experiments was not significant.

Field experiments

The field experiments were made on the Pockman ranch several miles north of Woodland, California, on a soil originally mapped in 1909 as Yolo clay loam. The soil contains calcium carbonate in the subsoil and, for this reason, is now classified as Sorrento clay loam.

Grain was planted on this field until 1946. In that year, it was first irrigated and planted to tomatoes, which produced 18 tons of fruit per acre. This crop received the first fertilizer used on the field; namely, 60 pounds of nitrogen from anhydrous ammonia and 300 pounds of 16-20-0 per acre.

The experimental field was planted to sugar beets of the U. S. No. 33 variety on March 24, 1947. The beets were thinned to a stand of approximately 90 plants per 100 feet of row on April 30. Each plot was 12 rows wide (20 inches between rows) and 598 feet long, comprising an area of 0.2746 acre per plot or nearly 10 acres for the 36 plots of the experiment.

Each of the six fertilizer treatments was assigned only once, at random, to each of the six plots of a block; and this randomization was repeated for each of the six blocks of the experiment. The fertilizers for each treatment (see table 2) were applied on May 7 and 8 as a sidedressing, 6 inches to one side of the plants and 5 inches below the soil surface.

The first water after fertilization was applied to the furrows in the soil the last of May. Thereafter the beets were irrigated periodically, and at no time were they observed to wilt.

The petiole samples were collected by walking 30 feet into the plot, taking four petioles (blades discarded) from the center four rows at this location, then walking 60 more feet into the plot and taking 4 more petioles, then 60 more feet, etc., until a total of 40 petioles had been collected at 10 separate stations within each plot. The leaf selected for the petiole sample was recently "matured" (13, 14) and was taken on each sampling date from a different competitive beet; that is, one surrounded by other beets at correct distances.

The preharvest beet weights and sugar determinations were estimated from the same plants as those used for the leaf samples. The final beet yields, however, were obtained by weighing the beets from each plot in trucks after they were hand-topped. Chemical methods were the same as those employed in the pot experiments.

The results for the field experiment were analyzed by the method of analysis of variance (9) as applied to plots randomized within blocks. The missing plot technique was employed to replace the values obtained for an untreated plot of high nitrogen nutrition and of high yield which occupied the space held by an open irrigation ditch during 1946. This calculated value was used whenever required in the computations of the analysis of variance and is included in the averages for the untreated plots given in tables 2 to 4 and figure 4.

EXPERIMENTAL RESULTS

Pot experiments

The average yields of roots and tops, sugar percentages, sugar produced, and nitrate values for the sugar beets of each treatment and their statistical evaluation are recorded in table 1. Although there is considerable variation in the individual values of a given treatment, as shown by the coefficient of variability, the trends are clearly indicated. The weights of the tops and roots increased considerably with each addition of nitrogen up to 1 or 2 gm. per pot; thereafter, no large changes in weight were observed. The nitrate concentrations of the petioles and blades, in contrast to the weights, failed to increase greatly until the soil received 1 or 2 gm. of nitrogen per pot. This relationship of nitrate in leaves to beet weight is clearly illustrated for "mature" petioles in figure 1.

TABLE 1

*Nitrate nitrogen of petioles and blades; sugar concentration of beets; weight of beets, tops, and sugar as related to nitrogen fertilization for the pot experiment**

NITROGEN ADDED	NITRATE NITROGEN†						BEET‡§ ROOT	SUGAR		TOPS‡	
	OP¶	MP¶	IP¶	OB¶	MB¶	IB¶				Fresh	Dry
gm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*gm.*	%	*gm.*	*gm.*	*gm.*
0.0	230	220	140	70	110	120	38	13.5§	5.1‡	76	12.5
0.25	230	220	110	60	90	140	38	13.4	5.2	116	17.0
0.50	560	450	130	70	110	130	55	13.2	7.3	166	24.3
1.00‖	2,660	3,040	580	340	450	210	85	13.2	11.2	261	34.6
2.00	24,500	20,000	8,700	4,200	4,470	2,830	71	10.2	7.2	396	43.7
4.00	29,300	26,200	14,000	6,100	8,100	5,500	90	9.5	8.6	472	51.7
6.00	33,500	29,800	16,800	7,200	9,600	7,500	87	9.0	7.9	414	43.9
8.00	31,600	26,800	15,100	8,600	10,500	7,500	67	9.3	6.2	399	45.7
L.S.D.**............	3,000	3,470	2,700	1,500	1,380	1,320	17	0.7	2.2	42	5.0
F-value††............	214.6	121.5	63.3	47.0	89.7	51.9	12.5	68.8	5.5	110.3	72.1
Coefficient of variability..............	14.6	19.4	28.4	33.3	24.4	32.5	19.8	4.9	23.5	11.2	11.3
General mean........	16,000	13,880	7,300	3,500	4,380	3,130	65.	11.3	7.1	289.	34.1

* Nitrogen was added to the soil as calcium nitrate. All treatments were replicated five times

† Dry basis.

‡ Weight per pot.

§ Fresh basis.

¶ OP = old petiole; MP = "mature" petiole; IP = immature petiole. OB = old blade; MB = "mature" blade; IB = immature blade.

‖ Average of three replications.

** L.S.D.—Least significant difference at the 5 per cent level. It should be noted that the L.S.D.'s as given are too small for comparison of the high mean values and too large for the low mean values. For example, the results for treatments 2.00, 4.00, 6.00, and 8.00, when analyzed as a group, do not differ significantly from one another for the dry weights of tops and fresh weights of beets. Conversely, the L.S.D.'s as given are too high for measuring the differences for the low mean values for treatments 0.0 through 1.00, which, upon separate analysis, indicate that each increase in the the dry or fresh weight of the tops is statistically significant.

†† The *F*-values required at the 5 per cent and 1 per cent levels are 2.34 and 3.30, respectively.

Here the weights increased gradually as more nitrogen was applied to the soil, while the nitrate concentrations of the petioles remained relatively low at a constant level. Then as more nitrogen was applied to the soil, the nitrate concentrations of the petioles and the beet weights increased simultaneously. As still more nitrogen was applied, the beet weights failed to increase greatly, even though there were tremendous increases in the nitrate concentration of the petioles. This same general relationship of nitrate concentrations to beet weights prevailed for the petioles or blades, whether old, mature, or immature leaves were selected for analysis. From the *F*-values (table 1), which are a combined measurement of the magnitude of the differences between treatments and the error within a treatment, the old petioles appear preferable for analysis to the recently "matured" petioles; and the latter appear better than the other plant parts in this series. Nevertheless, from practical considerations, such as ease of sampling and range of nitrate in the sample, the petiole of a recently "matured" leaf has been found more desirable for analysis than any other part of the plant studied thus far.

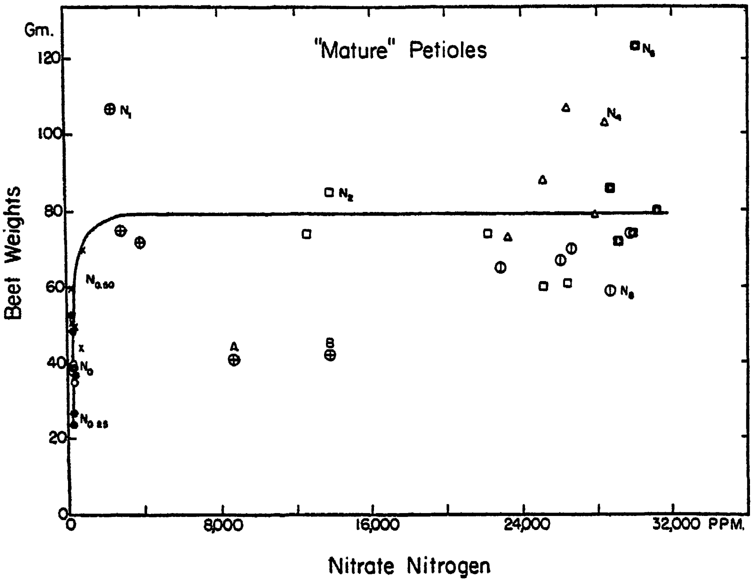

FIG. 1. BEET ROOT WEIGHT (FRESH BASIS) AS RELATED TO NITRATE NITROGEN CONCENTRATION (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES

N_1 = 1.0 gm. of nitrogen derived from calcium nitrate added in solution to each pot and is equivalent to 100 pounds of nitrogen per acre; all other symbols refer to fractions or multiples thereof. The solid line is a free hand curve drawn to fit the points as obtained. Points A and B are from plants that had been damaged by the larvae of moths.

From a study of the curves derived by plotting nitrate nitrogen values against beet weights, an approximate critical nitrogen value can be selected. The beet weights begin to decrease when this value is approximately 2,000 ppm. for recently "matured" petioles (fig. 1), 4,000 ppm. for old petioles (not shown) and 1,500 ppm. for immature petioles (not shown), whereas the value is about 1,000 ppm. for all ages of blades (fig. 2, mature blades only). Obviously, from the present data no sharp line of demarcation can be established to distinguish between an adequacy and an inadequacy of nitrate nitrogen of beets; but in spite of this gradual transition, a separation of deficient and nondeficient plants can be effected. Figure 1 shows that those plants with petioles having less than 1,000 ppm. of nitrate nitrogen gave weights distinctly less than those with more than 3,000 ppm. At the higher concentrations the beets failed to increase significantly in weight. The points A and B in figures 1 and 2 illustrate the general rule that when beet weights are low and the nitrate values are high, the decreases in growth that occur are most likely associated with causes other than a nitrogen deficiency, which for this experiment may have been due to the presence of cutworms which damaged a few of the plants during the course of the experiment.

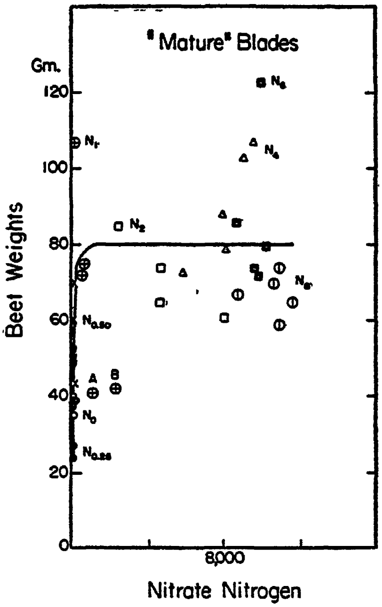

Fig. 2. Beet Root Weight (Fresh Basis) as Related to the Nitrate Nitrogen Concentration (Dry Basis) of Blades of Recently "Matured" Leaves

The symbols used in the graph are defined in figure 1.

The sucrose concentrations of the beets (table 1) are in accord with earlier observations in which sugar concentrations decreased as the nitrogen concentrations of the petioles (6, 11) or of the beet roots (4, 6, 8) increased. This general relationship is clearly shown in figure 3, in which sugar concentrations are plotted against nitrate concentrations of recently "matured" petioles. Beet plants that are low in nitrate content and are growing slowly accumulate sucrose in the roots until an average concentration of 13.5 per cent is attained for the untreated beet plants (table 1). When the plants are high in nitrate content and are growing rapidly, thus implying a rapid use of sugar for growth, the sucrose concentration of the beets tends to decrease until the average value is only 9.0 per cent for the beets receiving 6.0 gm. of nitrogen per pot. The beets of pots

A and B have intermediate nitrate and sugar concentrations, and in contrast to their nitrate yield relationship, these points lie on the curve as drawn in figure 3.

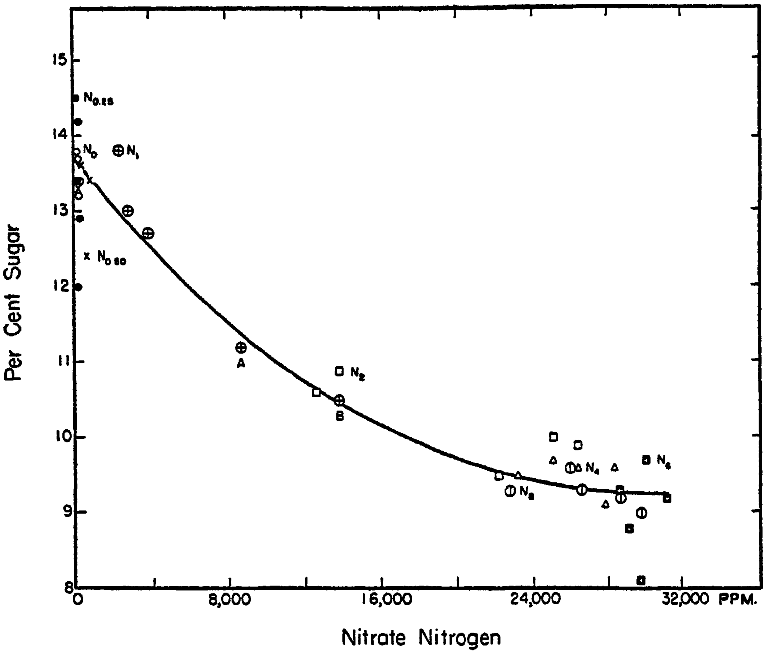

FIG. 3. RELATIONSHIP OF SUCROSE CONCENTRATIONS OF BEET ROOTS (FRESH BASIS) TO NITRATE NITROGEN CONCENTRATION (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES, AS OBSERVED IN THE POT EXPERIMENT

Here points A and B fall on the curve. The symbols used in the graph are defined in figure 1.

Field experiments

The results of the field experiments, including a statistical evaluation of the data, are presented in tables 2 to 4 and in figures 4 to 10. The nitrate values of recently "matured" petioles (tables 2), just as in the pot experiments, were in accord with the amounts of nitrogen applied to the soil. The lowest nitrate values were associated with the untreated plots, whereas the highest values were found with the highest additions of nitrogen. Experimentally, the effects of the treatments upon the nitrate concentration of the petioles were greatest early in the season (fig. 4). The magnitude of these effects in relation to over-all experimental error is reflected in the *F*-values recorded in table 2. The highest *F*-value of 53.9 occurred at the first sampling on June 10, and the lowest, 3.02, on September 23. In all cases these values were above 2.62, the 5 per cent level of significance; and in many instances they were greater than the 1 per cent level of 3.90.

The effects of nitrogen on the growth and sugar concentration of beets prior to the regular field harvest are summarized in tables 3 and 4. On June 24, 1947, the beet weights had not been affected significantly by the nitrogen fertilization (table 3), even though the nitrogen additions had increased greatly the nitrate concentrations of the petioles (table 2) and had significantly decreased the sugar concentration of the beets (table 4). From June 24 to July 30, the beet weights increased for all treatments but the increases for the beets fertilized with nitrogen were significantly greater than those that were untreated. A similar increase in the weights occurred from July 30 to August 28, but from the latter date to November 5, the weights remained constant (table 3). The sugar concentration of the beets increased for all treatments as the season progressed. Beets that were fertilized with more than 40 pounds of nitrogen per acre, however, were definitely lower in sugar concentration at all times (table 4), even though these beets had been deficient in nitrogen for some time prior to November 5 (table 2). The final yields of beets harvested from the entire plots are given in tons per acre in table 3 and are in general agreement with the yields obtained by pulling only 40 beets from each plot.

TABLE 2

*Nitrate nitrogen of petioles of recently "matured" leaves of sugar beets from the Pockman plots as influenced by nitrogen fertilization and time of sampling**

TREATMENTS†	JUNE 10	JUNE 24	JULY 16	JULY 30	AUG. 12	AUG. 28	SEPT. 9	SEPT. 23	OCT. 7	NOV. 5
	ppm.	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*	*ppm.*
Untreated	5,470	1,130	43	116	128	52	62	232	61	47
40N	10,700	3,620	1,100	452	358	33	62	185	78	67
80N	15,500	9,600	2,180	750	600	232	97	127	102	74
160N	19,500	13,700	5,600	4,670	2,410	1,790	590	760	404	143
240N	18,400	15,000	6,000	5,100	2,500	1,410	330	550	219	131
240N + P	19,700	14,700	6,500	5,200	3,530	1,630	1,400	590	286	171
L.S.D.‡......	2,260	2,430	1,270	1,340	1,520	820	640	437	192	72
F-value§.....	53.9	51.6	41.0	29.5	7.33	8.79	5.55	3.02	4.25	4.01

* Each nitrate nitrogen value represents an average of six plots consisting of 40 petioles per plot. The results are expressed on the dry basis.

† N = pounds of nitrogen per acre derived from ammonium nitrate and applied as a sidedressing on May 8 and 9, 1947. P = 200 pounds per acre of P_2O_5 derived from treble superphosphate applied at the same time.

‡ L.S.D.—Least significant difference at the 5 per cent level.

§ The *F*-values required at the 5 per cent and the 1 per cent levels are 2.62 and 3.90, respectively.

The relationship of nitrate nitrogen of the petioles to the growth of beets again may be illustrated conveniently by plotting the beet weight of each plot against its corresponding nitrate nitrogen value (figs. 5 to 8). The results for June 24 (fig. 5) show that even though there are tremendous differences in nitrate concentration of the petioles, there are no significant differences in beet root weights for any of the plots up to the time of this sampling. It is to be noted too that, even though a few of the nitrate values for the untreated beets had fallen below the critical nitrate nitrogen level and that the leaves of the untreated beets had just become a light green, insufficient time had elapsed to produce a significant decrease in growth of the beet plants. At a later date the beets with the petioles containing less than 1,000 ppm. of nitrate nitrogen had lower weights than the corresponding beets with higher nitrate levels.

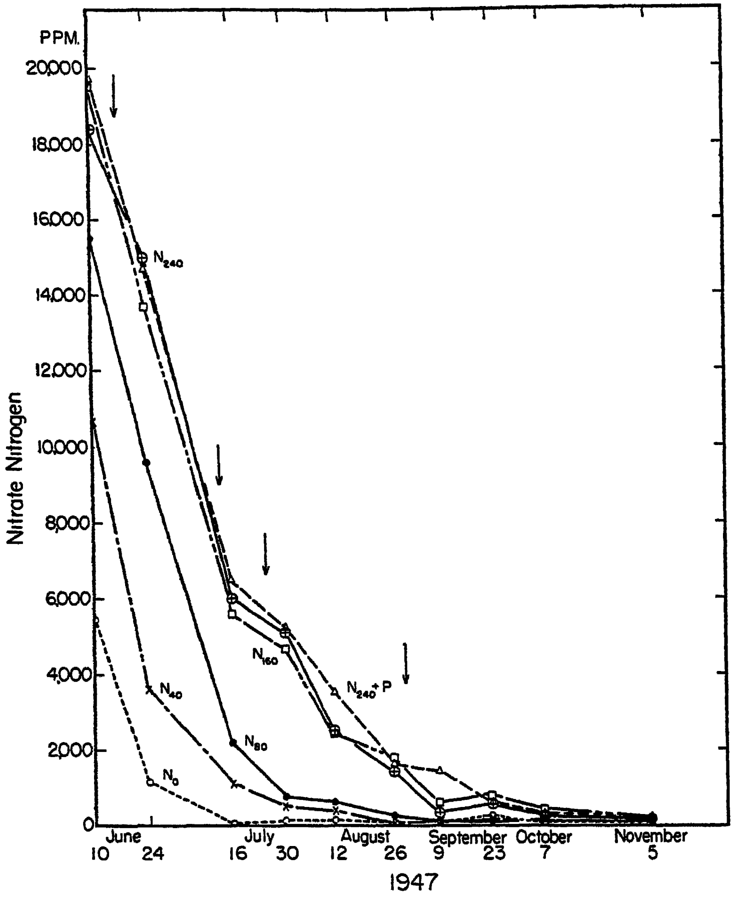

FIG. 4. NITRATE NITROGEN CONCENTRATION (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES OF BEETS GROWN IN THE POCKMAN FIELD AS RELATED TO NITROGEN FERTILIZATION AND DATE OF LEAF SAMPLING

N = pounds of nitrogen per acre applied as ammonium nitrate. P = 200 pounds of P_2O_5 per acre applied as treble superphosphate. The fertilizer was applied as a sidedressing on May 8 and 9 and irrigated thereafter for the first time the last of May. The dates of irrigation subsequent thereto are indicated by arrows.

The second set of beet and petiole samples were collected on July 30, 1947. The beet weights and nitrate values for this sampling are plotted in figure 6. The results clearly show that the untreated beets, which were low in nitrate

TABLE 3

*Weights of beet roots from the Pockman plots as influenced by nitrogen fertilization and time of sampling**

TREATMENTS†	JUNE 24	JULY 30	AUG. 28	NOV. 5	NOV. 10
	lb.	*lb.*	*lb.*	*lb.*	*tons*
Untreated	0.65	1.29	1.90	1.75	13.87
40N	0.71	1.50	2.06	2.02	15.76
80N	0.78	1.58	2.37	2.48	17.47
160N	0.78	1.92	2.48	2.78	19.16
240N	0.77	1.78	2.46	2.49	20.63
240N + P	0.75	1.80	2.50	2.75	19.95
L.S.D.‡	N.S.	0.25	0.25	0.34	1.35
F-value§	2.22	7.2	8.4	11.0	31.8

* Each value for the beet weights on June 24, July 30, August 28, and November 5 represents an average per beet of six plots consisting of 40 beets per plot. On November 10, 1947, the beets in each plot were topped by hand and weighed separately in trucks; each value again represents an average of six plots, in tons per acre.

† See footnote table 2.

‡ L.S.D.—Least significant difference at the 5 per cent level. N.S. = not significant.

§ The *F*-values required at the 5 per cent and 1 per cent levels are 2.62 and 3.90, respectively.

TABLE 4

*Sucrose percentage of beets from the Pockman plots as influenced by nitrogen fertilization and time of sampling**

TREATMENTS†	JUNE 24	JULY 30	AUG. 28	NOV. 5
	per cent	*per cent*	*per cent*	*per cent*
Untreated	12.00	15.61	15.91	15.97
40N	11.03	15.13	16.15	16.22
80N	10.10	14.15	15.52	15.38
160N	9.25	12.15	14.05	14.42
240N	9.50	12.20	13.90	14.47
240N + P	9.33	12.25	13.92	14.80
L.S.D.‡	0.72	0.54	0.47	0.59
F-values§	21.3	69.5	43.3	14.5

* Sucrose percentages of the beet roots are expressed on the fresh basis. Each value represents an average of six plots. A single sucrose determination of a 40-beet sample was made for each plot.

† See footnote table 2.

‡ L.S.D.—Least significant difference at the 5 per cent level.

§ The *F*-values required at the 5 per cent and 1 per cent levels are 2.62 and 3.90, respectively.

nitrogen on June 24 but did not differ in weight (fig. 5), are now significantly lower in weight (table 3) and are still lower in nitrate concentration (table 2) than those treated with nitrogen. The beets treated with 40 pounds of nitrogen

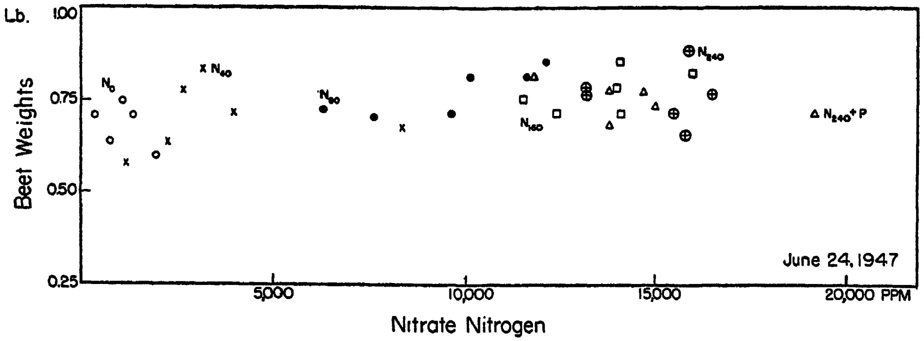

Fig. 5. Relationship of Beet Weight to Nitrate Nitrogen Concentration (Dry Basis) of Petioles of Recently "Matured" Leaves of Beets Collected from the Pockman Plots on June 24, 1947

On this date the beet weights do not differ significantly from one another, though there is a tremendous difference in the nitrate concentrations, thus suggesting that the nitrate values of the petioles may differ widely above the critical concentration (1,000 ppm. nitrate nitrogen) before affecting growth appreciably. The symbols used in the graph are defined in figure 4.

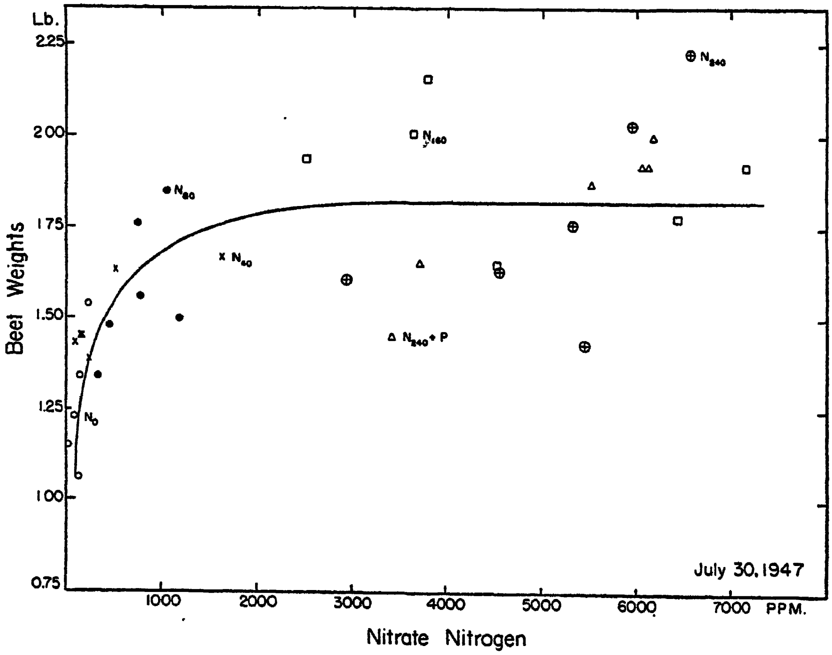

Fig. 6. Relationship of Beet Root Weight to Nitrate Nitrogen Concentration (Dry Basis) of Petioles of Recently "Matured" Leaves from the Pockman Plots for July 30, 1947

Beets with petioles of less than 1,000 ppm. of nitrate nitrogen tend toward significantly lower beet weights, whereas those above this value are well supplied with nitrogen and do not differ significantly from one another in weight. The solid line is a free-hand curve drawn to fit the points as obtained; the symbols used are defined in figure 4.

gave significantly higher weights than the untreated beets, but the nitrate values do not differ greatly from one another (fig. 6). Further increases in nitrate concentration and in beet weight occurred when the beets were fertilized with 80 or 160 pounds of nitrogen per acre. Still more nitrogen added to the soil increased the nitrate concentrations of the petioles well above 1,000 ppm., but now this had no effect upon the beet weights.

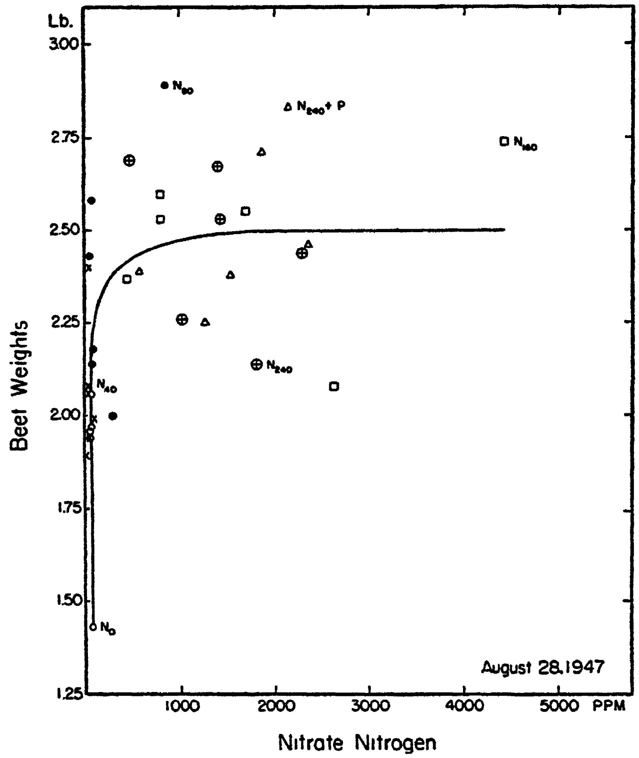

FIG. 7.

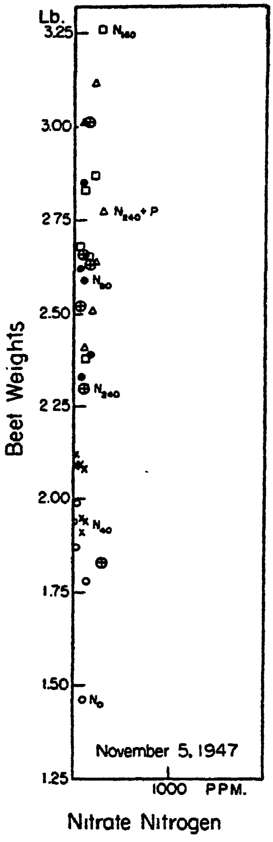

FIG. 8.

FIG. 7. RELATIONSHIP OF BEET ROOT WEIGHT TO NITRATE NITROGEN CONCENTRATION (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES FROM THE POCKMAN PLOTS FOR AUGUST 28, 1947

FIG. 8. RELATIONSHIP OF BEET WEIGHT TO NITRATE NITROGEN CONCENTRATION (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES OF BEETS COLLECTED FROM THE POCKMAN PLOTS ON NOVEMBER 5, 1947

On this date the nitrate nitrogen values of the petioles are consistently below 1,000 ppm. and do not differ appreciably from one another, whereas the weights increase in accordance with the nitrogen that was applied to the soil early in the growing season.

When the beets were sampled for the third time on August 28 (fig. 7), there were still more petioles virtually devoid of nitrate nitrogen, and at the same

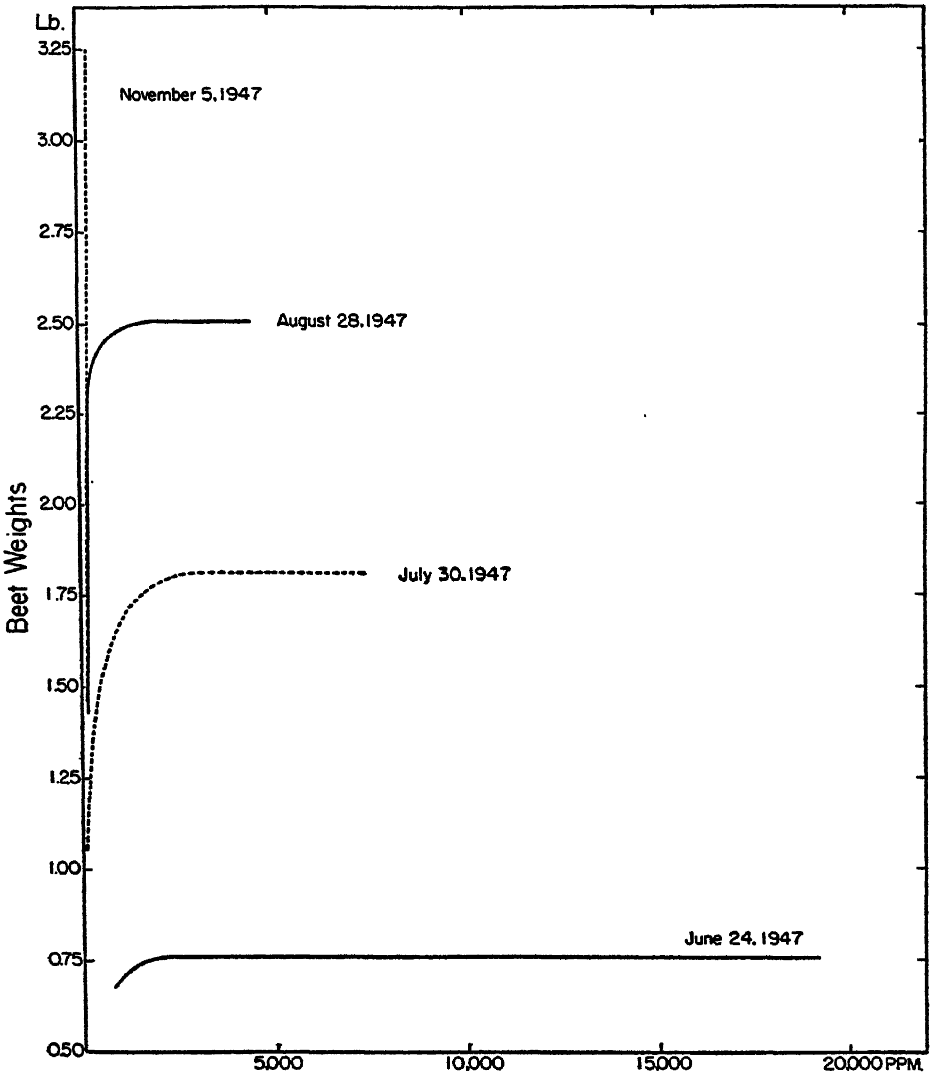

FIG. 9. SUMMARY OF FIGURES 5 TO 8 SHOWING THE GRADUAL TRANSITION OF BEETS WITH PETIOLES INITIALLY HIGH IN NITRATE CONCENTRATION, BUT NOT DIFFERING SIGNIFICANTLY IN WEIGHT (JUNE 24), TO BEETS DIFFERING GREATLY IN WEIGHT, BUT WITH VERY LOW NITRATE VALUES NOT DIFFERING APPRECIABLY FROM ONE ANOTHER (NOVEMBER 5)

Critical nitrate nitrogen values may be estimated from only the July 30 and August 28 samplings.

time there were more treatments that show significant increases in beet weight from the higher amounts of nitrogen added to the soil. When the petioles contained nitrate nitrogen at concentrations of 1,000 or more ppm., there were again no significant increases in beet weights. On the fourth and final sampling on November 5 (fig. 8), all nitrate values of the petioles were well below 1,000 ppm. and did not differ from one another greatly regardless of the amount of nitrogen previously added to the soil. The yields harvested from the entire plots, in contrast to the nitrate nitrogen values, increased significantly with all but the last increment of nitrogen applied to the soil (table 3). The final yields in this experiment were in proportion to the amount of nitrogen the beets could absorb from the soil during the growing season, and a measure of the adequacy or inadequacy of the nitrogen supply can be observed through successive petiole samplings. The gradual transition of the curves for nitrate plotted against beet weight which takes place during the growing season (figs. 5 to 8), is summarized schematically in figure 9.

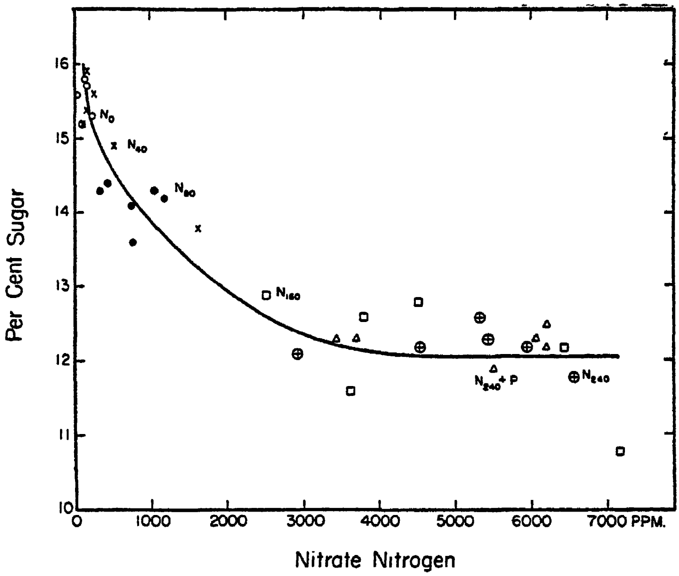

FIG. 10. RELATIONSHIP OF SUCROSE CONCENTRATIONS OF BEET ROOTS (FRESH BASIS) TO NITRATE NITROGEN CONCENTRATIONS (DRY BASIS) OF PETIOLES OF RECENTLY "MATURED" LEAVES AS OBSERVED IN THE POCKMAN FIELD EXPERIMENT ON JULY 30, 1947

The symbols used in the graph are defined in figure 4.

The relationship of nitrate concentration of the petioles to the sucrose concentration of the beets in the field experiment for July 30 is illustrated in figure 10. Just as in the pot experiment (fig. 3), the beets with high nitrate concentrations were low in sugar, whereas beets low in nitrate were high in sucrose.

DISCUSSION

Selection of the part of the plant that may serve as an indicator of its nitrogen status is subject to considerable difficulty and at times may be quite arbitrary. The *F*-values obtained in the pot experiment for the different plant parts (table 1) show that the highest values were associated with the old petioles and the second highest with the recently "matured" petioles. The coefficients of variability likewise favored these plant parts. From the standpoint of sampling under field conditions, it is much easier to sample the recently "matured" petioles than the old petioles; and furthermore, from the plant physiological point of view, the recently "matured" leaves play a much more important part in the life of the plant at the time of sampling than do the old leaves; and accordingly, the recently "matured" leaves are preferable to the old leaves for analysis, even though the latter appear somewhat better from the statistical point of view.

In determining the critical nitrogen level of plants, certain difficulties are encountered which are comparable to those present in an attempt to verify Liebig's law of the minimum, Blackman's concept of limiting factors, or Mitscherlich's idea that the effect of a given factor may be modified by other factors (1, 7). The crux of this problem lies primarily in the rate of change taking place in the zone of transition, starting from a direct increase in yield with each increment of the nutrient absorbed by the plant and proceeding to that of luxury consumption, where further increases in the internal concentration of a nutrient have no effect upon yield. This transition zone may be relatively narrow; as for example, when petioles or blades are analyzed for nitrate (figs. 1, 2, 13, 14) or petioles for phosphate (14); or may be relatively broad when blades are analyzed for phosphate (14) or when the entire tops of a plant are used for analysis. Though slight improvements in evaluating the data statistically may be made by increasing the number of observations taken in the transition zone, it is only through major improvements in experimental technique, along with a better understanding of the chemical processes taking place within the plant cells, that the true nature of the transition zone can be established.

In the present series of experiments the curves drawn in figures 1, 2, 6, and 7 were fitted to the data by inspection. It is doubtful whether the shape of the curves would have differed greatly had they been developed mathematically or if more points in the transition zone had been obtained. That the transition zone as drawn in the nitrate yield curves is approximately correct is indicated by applying the *F*-test to the separate zones of these curves. The *F*-test indicates that the beet weights from the untreated pots and those treated with 0.25 gm. nitrogen differed significantly from those receiving 0.50 and 1.00 gm. of nitrogen (also the latter two differed from each other); whereas this same test applied to the beet weights from the pots receiving 1 or more gm. of nitrogen indicates that the weights failed to differ significantly from one another. In contrast to the beet weight differences, the nitrate values for the "mature" petioles changed very little from the untreated to the 0.25 and 0.50 treatments, and thereafter the nitrate concentrations increased rapidly (fig. 1). In the field experiment these same relationships can be observed readily for the nitrate and beet weight values for July 30 (fig. 6 and tables 2 and 3). Here the zone of transition for the beet weights and nitrate values is between the 80- and 160-pound nitrogen applications. Use of regression coefficients on the data failed to define the transition zone more sharply than visual inspection or use of the *F*-test as discussed.

In estimating the critical nutrient level for a crop, the time of collecting the plant samples in relation to the nutritional responses observed is an important factor. In the pot experiment the beets were harvested when there were simultaneously large differences in growth between the beets receiving the smaller amounts of nitrogen and when there were no significant differences between the beets receiving the higher amounts of nitrogen. In this experiment, the critical nitrate nitrogen value was estimated to be somewhat less than 2,000 ppm. and probably somewhat greater than 0 for petioles from recently "matured" leaves. In the field experiment, estimations of the critical nitrogen level from the petiole and beet samples were made at four intervals during the growth of the beets. In the first set of beet and petiole samples, taken on June 24 (fig. 5), the nitrogen fertilization caused large differences in nitrate concentration of the petioles and no significant differences in beet root weights (table 3). On the basis of these observations, one might conclude incorrectly that there was no relationship between the nitrate concentration of the petioles and beet weights and that, therefore, the method of plant analysis was not a suitable means of evaluating the nitrogen status of the crop. The correct conclusion, as shown by the next two sampling dates (figs. 6 and 7), would be that some of the untreated beets had reached a low nitrate nitrogen level on June 24 and were already deficient in nitrogen, but that insufficient time had elapsed to decrease beet growth significantly. The correctness of this interpretation is clearly shown by the significantly lower beet weights in the untreated plots in all subesquent samplings. On the next two samplings, the curves obtained for nitrate plotted against beet weight (figs. 6 and 7) indicate the critical nitrogen level to be approximately 1,000 ppm. nitrate nitrogen or less. This is considerably lower than that indicated by the pot experiments and, accordingly, should serve as a basis for further study of this relationship in the field and in pots. On the last sampling date (fig. 8), just as in the first sampling on June 24, one would conclude from these results alone that no correlation exists between nitrate levels in the petioles and beet weights. Here the petioles were very low in nitrate, whereas the beet weights were increased greatly by the nitrogen fertilizations. The correct interpretation here would be that all the beets on the last sampling date were deficient in nitrogen in comparison to the known critical level, and accordingly would have grown more with still more nitrogen, provided no other deficiency appeared thereafter. Better yields from the 240 N treatment on this field would be contingent, in part, upon getting more phosphorus into the beets. This is indicated by an analysis of the petioles for phosphate (not reported here), which showed that the phosphate from the 240 N + P treatment failed to enter the beets in this experiment; and if some of it had been absorbed by the beets, then an increase in final yield might have been obtained, since the beets were low in phosphorus during a good part of the growing season. It is of significance to note too that from the final beet yields alone, the field would have been classified as adequately supplied with phosphorus; but from the petiole analyses, the beets were considered low in phosphorus and might have responded to this element had it been absorbed by the beet roots.

SUMMARY

Sugar beet plants were grown in pots of soil and in the field.

In the pot experiment, sugar beet plants fertilized with increasing amounts of nitrogen increased in top and beet root growth until the plants had received an adequate supply of nitrogen; thereafter, there were no significant weight increases. Analyses for nitrate nitrogen were made upon oven-dried plant material consisting of petioles and blades taken from old leaves, recently "matured" leaves, and immature leaves of these plants. Regardless of the plant part analyzed the plants were exceedingly low in nitrate nitrogen for the untreated soil and remained at this low level with each increment of nitrogen until the critical nitrate nitrogen level of the plant part was attained. Thereafter, large increases in nitrate took place within the plant part with each addition of nitrogen to the soil. Of the plant parts analyzed, the petioles from recently "matured" leaves appeared to be preferable. This preference is based primarily upon ease of sampling, upon wide range of nitrate nitrogen concentration—that is, from "zero" to almost 3 per cent on the dry basis—, and upon plant physiological considerations.

In the field experiment, the petioles from recently "matured" leaves gave somewhat lower critical nitrate nitrogen levels than in the pot experiments. Values of approximately 1,000 ppm. were obtained for field beets on July 30 and August 28 as compared to somewhat less than 3,000 ppm. for the pot experiment.

The results of the field experiment indicate that an estimate of the critical nutrient level of a crop must be made at a time when some plants have a deficiency and others have an abundant supply of the plant nutrient under study. Collection of the petiole samples prior to visible differences in growth resulted in large differences in nitrate concentration of the petioles but without any relationship to the observed beet weights. Conversely, when the plant samples were collected late in the season, it was again impossible to determine the critical nitrate nitrogen level of beets, for the plants were now devoid of nitrate even though the beet weights differed greatly and in accordance with earlier nitrogen fertilizations.

The nitrate concentration of the petioles at the start of the season in the field experiment were highest in the beets with the highest nitrogen fertilization. As the season progressed, differences between the nitrate values for the various treatments decreased gradually until several months prior to harvest, when all the values were approximately the same. In contrast to the nitrate values, the sugar concentrations increased gradually until harvested, whereas the beet weights increased until August 28 and thereafter failed to change appreciably.

The nitrate concentrations of the petioles in both pot and field experiments were correlated inversely with sugar concentrations of the beet roots; the higher the nitrate values, the lower the sugar concentrations.

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EFFECT OF BORON ON NITROGEN FIXATION BY AZOTOBACTER

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The essentiality of boron to higher plant life has been established, but the role of this element in the nutrition of microorganisms has not been widely studied. No evidence is available to indicate that boron is essential to bacterial growth. Brenchley (2) reported observations by several workers of poor development of nodule bacteria on roots of legumes that were boron deficient and thus were deprived of a normal accessory nitrogen supply.

Specific reference to the effects of boron on nitrogen fixation by *Azotobacter* is found in few instances throughout the literature. Voicu (14) reported that humus decreased the nitrogen-fixing power of *Azotobacter chroococcum* in presence of boron. When 100 mgm. of humus was present, the amount of nitrogen fixed decreased 60 per cent per 5 mgm. of boron and 85 per cent per 10 mgm. of boron. Horner and Burk (6) encountered difficulties in obtaining chemically pure compounds for nutrition studies with *Azotobacter*. They reported that in a magnesium-free medium, boron, among other elements, yielded no increase in growth of *Azotobacter*. Herzinger (5) reported growth of *A. chroococcum* in soil and culture solution of pH 6.8 to be optimum at a concentration of 0.3 ppm. boric acid.

The object of this experiment was to investigate the action of boron on *A. chroococcum*. Studies were made of the influence of boron on nitrogen fixation by *A. chroococcum* in field and greenhouse soils on agar plates. In addition, pure cultures of *A. chroococcum* were grown in agar and nutrient broth treated with boric acid at varying rates.

EXPERIMENTAL METHODS

Soils

The following soils were included in this study: Camas gravelly loam, Chehalis silty clay loam, Newberg sandy loam, Melbourne silt loam, and Klamath peat. The presence of *Azotobacter* in these soils was determined by Martin's (11) selective culture agar plate method.

Nitrogen in the soils was determined by a modified Kjeldahl procedure, and available soil boron was determined by the method of Berger and Truog (1).

Soil-inoculated agar plates were prepared as follows: The soils were air-dried and screened through a 20-mesh sieve. Half-gram portions of each soil were sprinkled on a nitrogen-free agar medium in 15-cm. petri dishes and incubated at 30° C.

Nitrogen and available boron contents of field samples of each of the five soils were determined. Then eight plates of each soil were incubated, and nitrogen was determined on half the plates after 4 days and on the remainder after 11 days. The results are shown in table 1.

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[1] Idaho Agricultural Experiment Station Research Paper 306.

In the fall of 1945, surface soil samples were taken from a series of plots at the Oregon State College Horticulture Farm that had been treated in spring with borax at rates of 20, 40, 80, 160, and 320 pounds per acre and from a control plot that received no borax. Available boron was determined on each sample. Soil-inoculated agar plates, 12 for each sample, were incubated. At 7, 14, and 21

TABLE 1

Nitrogen fixed in soils from field samples

Agar plates inoculated with soil

SOIL	SOIL REACTION	AVAILABLE SOIL BORON	PREINCUBATION NITROGEN CONTENT	NITROGEN FIXED	
				4 days	11 days
	pH	*ppm.*	*mgm.*	*mgm.*	*mgm.*
Camas gravelly loam..........	6.0	0.3	0.6	0.4	0.9
Chehalis silty clay loam.......	6.1	0.3	1.1	0.4	0.6
Newberg sandy loam..........	6.0	0.4	0.8	0.7	0.8
Melbourne silt loam...........	6.0	0.4	1.1	0.6	0.9
Klamath peat................	9.5	20.0	7.8	0.6	1.8

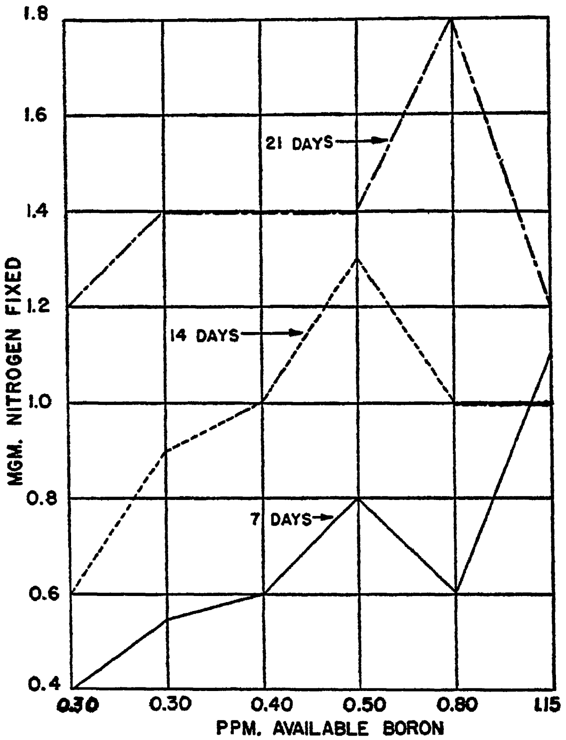

FIG. 1. EFFECT OF BORON ON NITROGEN FIXATION IN CHEHALIS SILTY CLAY LOAM

L. S. D. (0.01): 7 days—0.50; 14 days—0.09; 21 days—0.06 C. V. (per cent): 7 days—36.02; 14 days—4.63; 21 days—2.25.

days, nitrogen determinations were made on four plates of each sample. The results are plotted in figure 1.

Three soils—Newberg sandy loam, Chehalis silty clay loam, and Camas gravelly loam—from greenhouse studies[2] had received borax in treatments varying from 0 to 160 pounds per acre. Composite soil samples from replicated gallon jars in this experiment were handled in the manner previously described. Nitrogen fixation and available boron analyses are given in table 2.

TABLE 2

*Effect of boron on nitrogen fixation in different soil types**

Agar plates inoculated with soil

SOIL	RATE PER ACRE		AVAILABLE SOIL BORON	NITROGEN FIXED			
	Borax	Boron		7 days	Increase	14 days	21 days
	lb.	*lb.*	*ppm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*
Newberg sandy loam	Check	Check	0.4	0.25	—	0.35	0.35
	20	2.27	0.9	0.50	100.0	0.60	0.90
	80	9.08	1.2	0.60	140.0	0.80	0.75
	160	18.16	1.8	0.60	140.0	0.75	0.80
Chehalis silty clay loam	Check	Check	0.4	0.35	—	0.40	0.40
	5	0.57	0.6	0.70	100.0	0.75	0.85
	10	1.14	0.7	0.80	128.6	0.85	0.85
	20	2.27	0.9	0.75	114.3	0.80	0.80
	40	4.54	1.7	0.75	114.3	0.75	0.75
Camas gravelly loam	Check	Check	0.3	0.30	—	0.35	0.35
	10	1.14	0.5	0.65	116.7	0.85	1.10
	20	2.27	0.9	0.60	100.0	0.80	0.95
	40	4.54	1.2	0.60	100.0	0.70	0.75
	80	9.08	1.6	0.75	150.0	0.75	0.70
	160	18.16	2.0	0.55	83.3	0.60	0.60

* From greenhouse studies at Oregon State College, 1945–1947.

Laboratory media

Many microorganisms contribute to the nitrogen-fixing potential of a soil. Many of these were presumably present in the agar-plus-soil plates and therefore were affected by the boric acid treatments. To determine the effect of boron on *A. chroococcum*, pure culture methods were necessary.

Aqueous suspensions of *A. chroococcum* were plated on nitrogen-free agar and seeded to liter portions of nutrient broth. Both media were treated with boric acid at rates varying from 0 to 320 ppm. The agar plates were replicated 12 times per treatment. The experiments with both media were conducted three times, so that each treatment for each 7-day period was replicated 12 times in all.

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Both agar plates and nutrient broth cultures were incubated at 30° C. The nutrient broth cultures were shaken twice daily. At the end of each 7-day period for 3 weeks, four plates and four 50-ml. aliquots of nutrient broth from each treatment were withdrawn for nitrogen determination. In the nutrient broth cultures, pH and soluble boron were determined for each treatment after each 7-day period. Total boron was determined on the agar and the nutrient broth from the control cultures. Soluble boron determinations were possible only in the broth cultures. The results are recorded in figures 2 and 3.

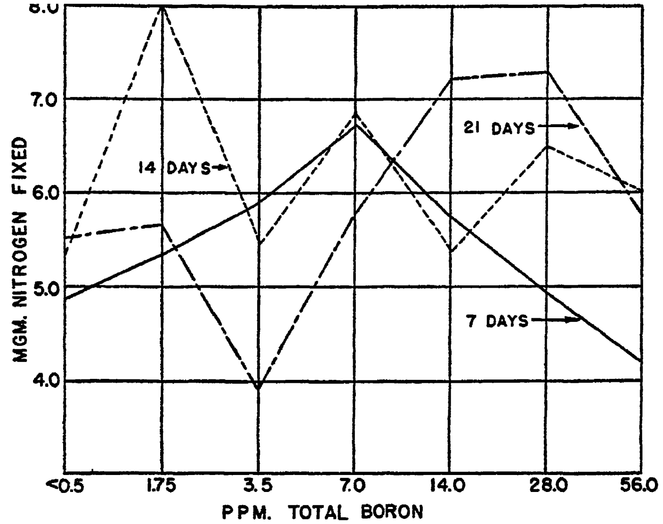

FIG. 2. EFFECT OF BORON ON NITROGEN FIXATION ON AGAR PLATES BY *Azotobacter chroococcum*

L. S. D. (0.01): 7 days—0.20; 14 days—0.20; 21 days—0.16 C. V. (per cent): 7 days—3.20; 14 days-2.77; 21 days—0.98

Detection of ammonia nitrogen from agar cultures

The experiments with the two laboratory media described above were each repeated three times. In each case the nitrogen values followed the pattern illustrated in figures 2 and 3. Nitrogen values for the 7-day cultures rose steadily to maximum values, then fell off steadily. Nitrogen values for the 14- and 21-day cultures followed an irregular path. In several instances, apparently the modified Kjeldahl analysis did not account for all the nitrogen in these samples or nitrogen was being lost as ammonia from the cultures during incubation. One example of this is found in figure 2 where the nitrogen value is only 3.92 mgm. for the 21-day-old agar plates which had been treated with 3.5 ppm. boron.

To determine whether nitrogen was being lost as ammonia, nitrogen-free agar carrying 3.5 ppm. boron as boric acid was inoculated with *A. chroococcum*. This was shaken in a sterile 5-liter vacuum flask until the solidified agar gave a maximum of surface for bacterial growth. This surface was equal to at least the combined area of twelve 15-cm. petri dishes. An inlet tube carried filtered and washed air into the flask, as illustrated in figure 4. The outlet carried the atmosphere

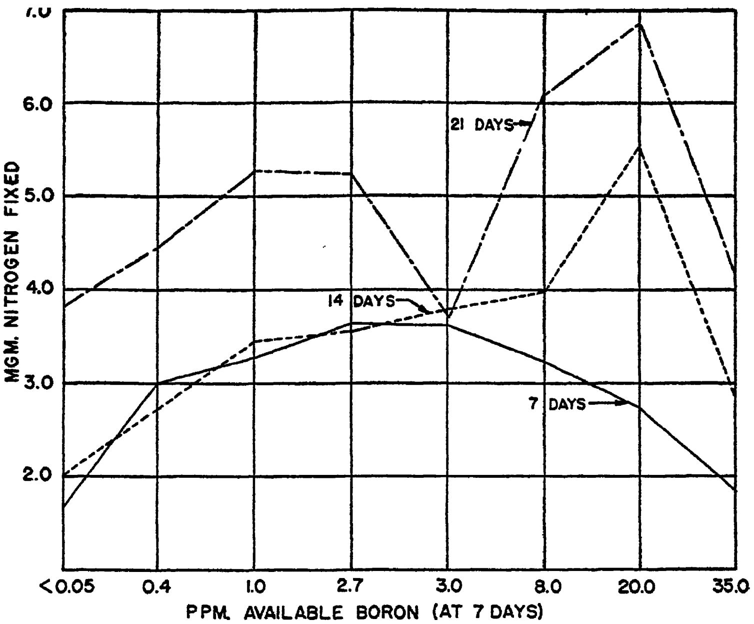

FIG. 3. EFFECT OF BORON ON NITROGEN FIXATION IN BROTH CULLURES BY *Azotobacter chroococcum*

L. S. D. (0.01): 7 days—0.07; 14 days—0.21; 21 days—0.33 C. V. (per cent): 7 days—2.40; 14 days—5.73; 21 days—2.03.

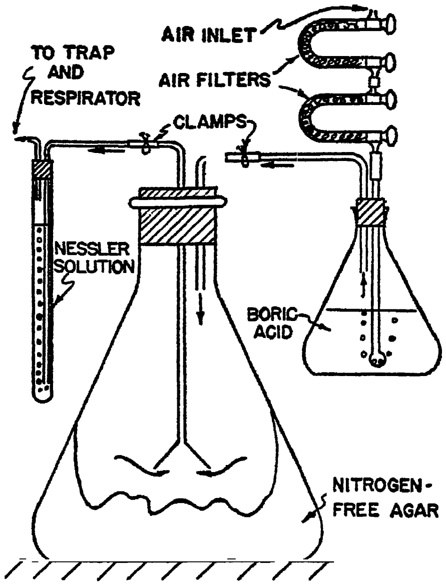

FIG. 4. UNIT FOR DETECTION OF AMMONIA NITROGEN

from the culture flask under suction through a 12-inch column of Nessler solution. In this manner a constantly changing atmosphere was maintained in the culture flask and all outgoing air was checked for ammonia content. All parts of the apparatus were originally sterilized, and after a month's operation there was no contamination evident in the agar culture. A second agar unit was run at the same time as a check in which no organisms were cultured. The Nessler solution on both units was renewed once a week. Room temperature varied from 25° to 30° C. during the test. During the 4 weeks' operation of these two units, no ammonia appeared to be released from either the culture flask or the control flask.

RESULTS AND DISCUSSION

Soils

The results shown in table 1 and figure 1 and observations described below indicate that *A. chroococcum* is one of the nitrogen-fixing organisms present in the soil samples examined. In every case nitrogen values increased in the 4-day-old and 11-day-old agar plates inoculated with soil. The pH of these samples ranged from 6.0 to 9.5 and available soil boron from 0.3 to 20 ppm. Colonies developing on these plates were clustered around soil particles or granules. They had a white, glistening, and gummy appearance. Microscopic examination revealed oval or fat rod-shaped nonmotile organisms. Colonies were inoculated on nitrogen-free agar slants. The original white growth became brown after 2 weeks' incubation. After 14 days' incubation, a floating membrane formed in tap water cultures containing 2 per cent mannitol and 0.02 per cent dipotassium phosphate inoculated with 0.5 gm. of soil.

The figures in table 2 show evidence of a relationship between available soil boron and nitrogen fixation. Borax applications to the Newberg, Chehalis, and Camas soils increased the available boron from 0.4, 0.4, and 0.3 ppm. respectively in the checks to maxima of 1.8, 1.7, and 2.0 ppm. in the treated soils. Nitrogen fixation on these treatments increased 83.3 per cent to 140.0 per cent over the checks in the 7-day plates inoculated with soil. In the 14-day and 21-day plates, the highest nitrogen increases were found within the available boron range of 0.5 to 0.9 ppm. This includes the optimum range of 0.5 to 0.75 ppm. reported by Jordan and Powers (7), for medium-textured soils in greenhouse trials using Bountiful beans as the indicator crop.

Figure 1 indicates that a significant increase in nitrogen fixation occurred in the 7-day plates when the available soil boron was increased from 0.30 ppm. to 0.50 ppm.; in the 14-day plates when there was no apparent increase in available boron and in the 21-day plates when the available soil boron rose to 0.80 ppm.

Seven-day cultures

The effect of boric acid treatments on pure cultures of *A. chroococcum* is shown in figures 2 and 3. In the 7-day-old agar plates, nitrogen increases amounted to 20.8, 38.2, and 18.2 per cent in the agar treated with 3.5, 7.0, and 14.0 ppm. boron respectively. On the 7-day curve in figure 2, as the total boron increases to 7 ppm., there is a highly significant increase in nitrogen fixation at the 1 per cent level. With higher boron concentrations, nitrogen fixation decreases.

In the 7-day-old broth cultures, replicates carrying 2.7 and 3.0 ppm. soluble boron were not significantly different in nitrogen content. These nitrogen values were 3.63 and 3.61 mgm. and were maximum values, as shown in figure 3. Successive nitrogen values on this curve are significantly different at the 1 per cent level, with the exception mentioned. Smaller amounts of nitrogen were fixed in the nutrient broth cultures than in the agar plates. Percentage increases in nitrogen values, however, were greater in the treated nutrient broth cultures. Nitrogen increases declined significantly in both agar and nutrient broth cultures carrying more than 7 ppm. total boron (at the 3.0 ppm. available boron level in figure 3). The relatively small increases in available or soluble boron in the cultures with successive doubling of the amounts of boron added may be attributed to fixation. In this case, the excess calcium carbonate present in the culture media tends to tie up part of the total boron present. Overliming causes a similar phenomenon in soils (13).

The nutrient broth cultures were analyzed for available boron. For the 7-day-old cultures in which 0.4 ppm. of soluble boron was present, the nitrogen increase was significantly greater, 78.57 per cent, than in the check culture carrying less than 0.05 ppm. soluble boron. Above 3 ppm. soluble boron, nitrogen fixation declined.

Fourteen- and twenty-one-day cultures

Nitrogen values of 14-day-old and 21-day-old cultures in both agar and nutrient broth were erratic, as shown in figures 2 and 3. This may be attributed to at least three factors: (*a*) cell decomposition in old cultures resulting in partial nitrogen loss as ammonia; (*b*) nitrogen lost as ammonia during incubation in cultures at certain boric acid concentrations; (*c*) failure of the modified Kjeldahl procedure to account for all the nitrogen present. Kostytschew and co-workers (8, 9) reported finding ammonia in filtrates from cultures of *Azotobacter agile.* They stated that the ammonia was an intermediary in fixation rather than due to cell decomposition. In 1930, Winogradsky (16) demonstrated that *Azotobacter* cultures readily formed ammonia when grown on silica gel medium containing lactate or succinate. Other workers, including Burk and Horner (3) have disagreed with the above reports.

The absolute values of the nitrogen determinations obtained for 14-day-old and 21-day-old cultures may be open to question. Smyth and Wilson (12), McKibbin *et al.* (10), Christensen and Fulmer (4), and others have reported that nitrogen found by Kjeldahl modifications in biological materials is less than that indicated by the Dumas absolute method. Wilson (15) concluded that in experiments in which the development of an organism changes the form of nitrogen, apparent gains and losses may reflect only the ability of a given Kjeldahl method to estimate different types of nitrogenous compounds.

Although the nitrogen values are erratic for the 14-day-old and 21-day-old cultures at the various boron levels, the great majority of the values are significant. Analyses of these cultures indicate that more nitrogen is fixed in the cultures treated with boric acid than in the control cultures that had received no boric acid.

SUMMARY AND CONCLUSIONS

Azotobacter chroococcum was among the nitrogen-fixing organisms present in Camas gravelly loam, Chehalis silty clay loam, Newberg sandy loam, Melbourne silt loam, and Klamath peat. Available boron and pH of these soils varied from 0.3 to 20 ppm. and from 6.0 to 9.5 respectively.

The Camas, Chehalis, and Newberg soils, when treated with borax at rates up to 160 pounds per acre and plated on nitrogen-free agar, gave increased nitrogen values over the untreated soils, which contained 0.3 to 0.4 ppm. available boron. These increases amounted to 100 per cent or more in the treated soils when the available boron ranged from 0.5 to 1.8 ppm.

Seven-day-old agar plates inoculated with Chehalis silty clay loam gave significant increases in nitrogen values where the available boron was increased from 0.3 ppm. to 0.5 ppm.

Agar plates inoculated with *A. chroococcum* and treated with boron varying from 0 to 56 ppm. showed significant increases in nitrogen content up to 7 ppm. total boron. At this point, nitrogen fixation declined.

Broth cultures inoculated with *A. chroococcum* and treated with 0 to 56 ppm. of boron showed significant increases in nitrogen content after 7 days in cultures carrying up to 3.5 and 7 ppm. total boron. Cultures carrying more than 7 ppm. total boron or 3 ppm. available boron fixed smaller amounts of nitrogen.

Nitrogen determinations of 14-day-old and 21-day-old cultures followed an irregular pattern, in contrast to the 7-day-old cultures. The erratic values indicate that either nitrogen was lost as ammonia or that the modified Kjeldahl procedure gave values that were too low for nitrogen. No loss of ammonia from the cultures could be demonstrated.

Although nitrogen values might not be regarded as absolute, the boron treatments in soils and the boric acid treatments in pure cultures seemed to increase nitrogen fixation by *A. chroococcum*.

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BORON SOURCES OF MODERATE SOLUBILITY AS SUPPLEMENTS FOR SANDY SOILS

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Differences in solubility of various boron supplements can cause important differences in their effects upon the growth of economic plants. Borax, one of the most soluble, came into inadvertent but widespread use as an impurity in domestic potash fertilizers during World War I. Its effects appear to have been more harmful than beneficial. The first toxicity was noted in 1917 on fields of corn in the vicinity of Francesville, Indiana (12, pp. 16, 17). Conner and Fergus (1) found that ½ to 4 pounds of anhydrous borax per acre when drilled with corn seed caused serious injury. Morse (7) reported material losses in Maine potato fields in 1919; and Plummer and Wolf (11) pointed out that in North Carolina the yields of cotton and tobacco were greatly decreased. It was observed (11; 12, pp. 16, 17) that fertilizers containing borax caused most severe injury in areas of light sandy soils.

Later, several investigators found boron in minute amounts to be essential for growth and quality in various economic plants. Johnston and Fisher (3) pointed to the necessity for a limited but constant supply throughout the growing season. Eaton (2) in 1932 suggested that Colemanite, a less soluble boron source than borax, might be used advantageously. McHargue and Calfee (6) in 1933 reported that in greenhouse pot experiments a powdered borosilicate of low solubility was superior to the soluble borates for lettuce. Muckenhirn (8) also used borosilicate successfully in quartz sand cultures. These reports directed attention toward boron sources of low solubility somewhat before borax came into general use as a soil supplement.

Aside from its possible toxic effects, borax is an inferior boron source for sandy soils because of its rapid loss by leaching. Laboratory studies by Krügel, Dreyspring, and Lotthammer (4) on the rate of leaching of various boron sources gave the following results: From a borax-superphosphate mixture used on a slightly humic loamy sand, 83.3 per cent of the applied boron was lost by leaching with water equivalent to about 28 inches of rain. On the other hand, magnesium-boracite was not subject to leaching even on light soils. Under field conditions, with borax as the source, the writer (17) found as low as 1.94 per cent of the applied boron remaining in Lakeland fine sand, determined as boiling-water extractable boron in the 0–6 inch zone after 4 months and 16.5 inches of rain. Practical aspects of rapid loss by leaching were noted by White-Stevens (16), who reported that borax in amounts adequate for vegetable production in normal years became insufficient in years of heavy rainfall. He suggested that the amount required in a dry season be applied each year, then in the event of excessive rains, more borax be used in sidedressings with nitrate of soda or mixed into fungicidal sprays.

Lynch (5) found that in the conventional method of drilling a fertilizer-borax mixture with the seed, the amount of borax required to give full control of brown heart of rutabagas impaired germination and severely injured emerging seedlings. This injury took the form of white or yellow cotyledons and stunted growth. Such seedlings were easily killed by dry weather or adverse growing conditions; and in surviving plants yields were likely to be seriously reduced. As an alternative, broadcasting at the rate of 40 pounds of borax per acre gave good control in normal years, but in years of heavy rainfall the borax was leached, allowing serious incidence of brown heart. Lynch's conclusion was as follows:

> The production of a compound of boron which can be safely drilled with the seed to control brown heart without affecting germination should be the first objective. The acreage annually devoted to turnips and swedes and the widespread and often severe losses caused by the disease undoubtedly justify the carrying out of additional research.

The primary source of boron in humid soils is the mineral tourmaline which, according to Whetstone, Robinson, and Byers (15) is the only boron mineral commonly identifiable in soils. This complex aluminum-borosilicate contains 10 per cent or less B_2O_3, or about 3 per cent boron. It is highly insoluble, as will be seen in the following comparison between the total and water-extractable boron content of Florida soils. Spectrographic analyses reported by Rogers *et al.* (14) showed that Florida mineral soils have an average total boron content of about 70 ppm. The boiling-water-extractable boron (17) is about 0.10 ppm. Thus, for every 700 parts of total boron, only about 1 part is in readily soluble form. Plant roots in these soils are accustomed to soluble boron in extremely small amounts.

From the foregoing it would appear that where boron supplements are needed, some effort should be made to select those which will furnish a low and fairly constant supply in the soil solution. The only record noted of borosilicate as a source was in the references already mentioned; however, Colemanite was employed recently in pot experiments by Page and Paden (10), who found that over a period of 26 days it was much less soluble than several other domestic borates. No record has been found of systematic investigation of the less soluble boron sources in the field.

The present experiments were designed to study in the field several domestic boron carriers of diverse solubility, to establish practical criteria for their use as soil supplements. Only materials likely to become available in adequate commercial supply were used.

MATERIALS

1. Borax: $Na_2B_4O_7 \cdot 10H_2O$. The commercial grade used was listed as having a purity of 99.5 to 100 per cent. The B_2O_3 content is approximately 36.5 per cent; hardness, 2 to 2.5: specific gravity, 1.70.

2. Fertilizer borate: A semirefined commercial product containing 34 per cent B_2O_3. Physical properties similar to those of commercial borax.

3. Kernite: $Na_2B_4O_7 \cdot 4H_2O$. Occurs as long fibrous prismatic crystals, colorless to white. B_2O_3 content 51 per cent. Similar to borax in chemical composition, but varies markedly in its physical properties. Fineness of grinding: 16 meshes (per inch) and finer. Hardness, 3.0; specific gravity, 1.95.

4. Colemanite:[1] A hydrated calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$. Occurs as colorless to white short prismatic crystals, usually highly modified and imbedded in masses of less pure material. B_2O_3 content of pure crystals about 50 per cent; that of commercial grades about 28 to 44 per cent. Fineness of grinding in the different experiments: part A, 60 mesh and finer; Part B, 20 mesh and finer; and part C, 20–40 mesh. Hardness, 4 to 4.5; specific gravity, 2.42.

5. Borosilicate: A synthetic material containing about 13 per cent B_2O_3. Ground to 20 mesh and finer for part B; and to 100 mesh for part C.

ANALYTICAL

Plant analysis for boron was by the foliage extraction micromethod (18) which had been found satisfactory in evaluating small differences in boron uptake by collards. Boron in the soil was determined as boiling-water extractable, by a modification of the method of Naftel (9). The details were as follows:

10 gm. of air-dried soil was extracted by boiling with 50 ml. of water in a 250-ml. boron-free flask attached to a boron-free reflux condenser. After 5 minutes of boiling, the heat was removed and the flask and contents were allowed to cool about 15 minutes, then placed in a refrigerator until reduced to room temperature. The supernatant solution was then poured immediately into an 80-ml. cellulose-nitrate centrifuge tube to fit the Sorvall Type SP angle centrifuge, run at 3700 r.p.m. for 25 minutes, then allowed gently to come to a stop. Approximately 25 ml. of the clarified solution was transferred into a similar cellulose-nitrate tube by means of a pipette with a rubber tube extension. This solution was stirred, and two 10-ml. aliquots were removed for duplicate analyses.

The reagents were the same as those employed for determining boron in plant tissue. In soils analysis accuracy was improved by removing the evaporating dishes from the steam bath at the end of the first evaporation as soon as they reached approximate dryness. Use of filter paper was avoided, to prevent boron contamination (18). Although the values for native water-soluble boron in the soils presented herein may appear low in comparison with those published elsewhere, they are in agreement with the values reported by Rogers (13) for similar soils in Albama.

EXPERIMENTAL

The three phases of the experiment were designated as parts A, B, and C. All were on Lakeland fine sand, a soil of low general fertility, with a reaction level, before adjustment, of about pH 5.6. Parts A and B were conducted on a plot area where the soluble boron content in the 0–6 inch depth was 0.08 ppm.; part C was with topsoil transported, sieved, roughly homogenized, and placed to a depth of 16 inches in 3- by 3-foot bottomless concrete pits in which the original subsoil (also Lakeland) was retained. The soluble boron in the soil of part C was 0.03 ppm., an unusually low value.

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[1] Colemanite is mined and processed by the Pacific Coast Borax Company, Los Angeles 14, California; the 100-mesh Borosilicate, No. 7740, is produced by the Corning Glass Works, Corning, New York.

Part A included all four of the California borates (materials 1 to 4). The log was as follows:

1947
Nov. 6 Broadcast 1,500 pounds of dolomite per acre, which contained sulfates of copper, manganese, and zinc at the rate of 20, 25, and 7½ pounds per acre, respectively; also the boron supplements to give 20 pounds borax-equivalent per acre, using randomized plots in triplicate.
Nov. 7 Rain, 1.53 inches.
Nov. 10 Applied 5-7-5 fertilizer, 500 pounds per acre, made up from uramon, superphosphate, and muriate of potash.
Nov. 11 Rain, 0.77 inch.
Nov. 13 Rutabaga seed planted.
Nov. 14 Collard plants set.
Dec. 14 Rainfall, first month, 1.08 inches.
1948
Jan. 12 Applied second and final 500 pounds of fertilizer per acre.
Jan. 14 Rainfall, second month, 2.15 inches.
Feb. 14 Rainfall, third month, 6.59 inches.
Mar. 14 Rainfall, fourth month, 8.75 inches.
Mar. 15 Collards harvested.
Mar. 16 Soil sampled for residual boron.
Mar. 18 Rutabagas harvested.

The soil reaction averaged pH 6.1, this level having resulted from the dolomite application. At harvest, the rutabagas grown without boron supplement, especially those of marketable size, showed notable boron-deficiency symptoms. All four of the boron supplements appeared equally effective in correcting this deficiency; however, the yield was considerably reduced by the two sources of greatest solubility. The results of analysis of the soil for water-soluble boron and the yields of the crops are given in table 1.

The results indicate striking differences in the amounts of boiling-water-extractable boron remaining in the top 18 inches of soil from the various supplements. The California borates fall into two classes: the extremely soluble borax and fertilizer borate, and the somewhat less soluble Kernite and Colemanite. From these two latter materials more than twice as much of the applied boron was retained as from borax and fertilizer borate. With borax and fertilizer borate there was notable repression of yield; with the same amount of boron applied in the form of Kernite and Colemanite, this repression did not occur. The only tenable interpretation is that of early season injury from too high a concentration of boron in the soil solution where the rapidly soluble borax and fertilizer borate were used.

On April 14, 1948, a new experimental unit was begun as a preliminary test of boron supplements of a wider range of solubility than previously studied. Borax was used to represent rapid solubility; Colemanite, the least soluble of the domestic borates, to represent moderate solubility; and 20-mesh borosilicate, a highly insoluble material, to represent slow solubility. In this experiment, designated as part B, the test crop was hairy indigo (*Indigofera hirsuita* L.). Borax and Colemanite were used at 10, 20, and 40 pounds per acre; the 20-mesh borosilicate was applied at rates of 50, 100, 200, and 400 pounds per acre. No fertilizer was applied.

Because of very dry weather the seeds of the hairy indigo did not germinate until late in May, when their emergence was assisted by several rains. By mid-June differential toxicity effects were noted: the most severe was from 40 pounds of borax, while 20 pounds also showed injury. The symptoms from borax and Colemanite were quite different: borax gave an almost immediate effect, apparently by injury to the roots, with notable stunting of the tops; Colemanite, on the other hand, had no serious initial effects upon growth, but its effect showed up later as a typical marginal burn of the foliage. In the borax plots essentially no marginal burn developed, yet the plants in the 40-pound borax treatments remained dwarfed throughout the growing season. The reason for failure to develop the foliage symptoms usually associated with boron toxicity appears to be as follows: the rapidly soluble borax injured the rootlets immediately so they were incapable of performing their normal uptake functions, then the summer rains leached the soluble boron rapidly away, and when the roots were able to resume normal activity the boron supplement had been depleted to an amount insufficient to produce the usual marginal burn in the foliage. With Colemanite the rate of solution appears to have been sufficiently slow initially that normal root systems developed which later took up boron from this progressively-dissolving material until marginal burn was produced in the foliage. Analysis of the foliage on August 4 furnished data which support the above premise, as the leaves from the borax treatments of 10, 20, and 40 pounds per acre showed, respectively, 0.28, 0.32, and 0.26 γ of boron per 10 sq. cm. of leaf;

TABLE 1

Boron retention in Lakeland fine sand from four sources of boron, and associated yields of vegetables

20 POUNDS BORAX-EQUIVALENT PER ACRE, AS	DEPTH SAMPLED	BORON FOUND	BORON RETAINED		GREEN WEIGHT COLLARDS	GREEN WEIGHT RUTABAGAS
	in.	*ppm.*	*ppm.*	*per cent*	*gm.*	*gm.*
(No boron supplement)	0–6	0.08	—	—	3146	2860
	6–18	0.04	—	—		
Borax	0–6	0.12	0.04	3.5	2160	1755
	6–18	0.10	0.06	10.6		
Fertilizer borate	0–6	0.12	0.04	3.5	2481	2690
	6–18	0.08	0.04	7.1		
Kernite	0–6	0.16	0.08	7.1	3246	3515
	6–18	0.14	0.10	17.6		
Colemanite	0–6	0.20	0.12	10.6	4008	3126
	6–18	0.14	0.10	17.6		

whereas leaves from the corresponding Colemanite treatments showed the respective values of 0.42, 0.56, and 0.74 γ. The plants were harvested on August 11, and the yields are given in table 2. With borax at 40 pounds per acre, injury was much more severe than with Colemanite at the same rate, for the yield as compared with the check was reduced 78 per cent by borax, but only 25 per cent by Colemanite. Borosilicate produced no visible symptoms of injury, but the yield was reduced at the 200- and 400-pound rates of application.

From a practical standpoint, 20-mesh borosilicate was regarded as too coarse and too insoluble, necessitating too large an application per acre to make it economical. For part C, therefore, borosilicate ground to pass 100 meshes per inch was obtained. This was used as before in comparison with borax and Colemanite, which were applied at 5, 15, and 45 pounds per acre; whereas the borosilicate was used at 30, 90, and 270 pounds per acre. The log was as follows:

TABLE 2

Yield of hairy indigo grown on Lakeland fine sand as influenced by boron supplements of diverse solubility

BORON SOURCE		PLANT YIELD
	lb./A.	*gm.**
(Check plots)	0	2837
Borax	10	2860
Borax	20	1837
Borax	40	633
Colemanite	10	2719
Colemanite	20	1840
Colemanite	40	2135
Borosilicate	50	2913
Borosilicate	100	3549
Borosilicate	200	2356
Borosilicate	400	2158

* Green weight; mean of three replications.

1948

Dec. 23 Broadcast 500 pounds of 5-7-5 fertilizer (same as for part A) which contained sulfates of copper, magnesium, manganese, and zinc to give 25, 100, 25, and 10 pounds per acre, respectively. The boron materials also were mixed into this fertilizer, just before application. Limestone at 1,500 pounds per acre had been used 2 years previously; the reaction, except for check omissions, was pH 6.5.

Dec. 24 Planted seeds of collards and rutabagas, the collards as a source of foliage for periodic analysis.

1949

Jan. 3 Collards coming up well, except where 45 pounds of borax per acre was applied.

Jan. 17 No injury as yet from Colemanite or borosilicate in their highest amounts (45 and 270 pounds per acre, respectively).

Jan. 19 Conditions in collards photographed (figs. 1 and 2).

Collards Foliage for Periodic Analysis

	SAMPLING PERIOD	WEEKS PLANTED	INCHES RAINFALL IN PERIOD	INCHES RAINFALL, TOTAL
Jan. 24	First	4½	1.03	1.03
Feb. 14	Second	7½	5.54	6.57
Mar. 7	Third	10½	1.82	8.39
Mar. 28	Fourth	13½	1.40	9.79
Apr. 21	Fifth	17	9.96	19.75

On January 24, month after the seeds were planted, foliage samples from the collards were gathered and analyzed for boron. The results of these and subsequent analyses are given in figure 3. The graphs illustrate clearly why initial injury is so often experienced with borax. In the leaves grown with borax as the source as compared with those grown with Colemanite, the ratio of boron was 8 to 1 at the 5-pound-per-acre rate, 5.8 to 1 at the 15-pound rate, and 9.2 to 1 at the 45-pound rate. The values for Colemanite did not long remain at their initial low level, for by the next period of analysis, only 3 weeks later, the foliage boron from Colemanite had exceeded the level from borax at both the 5- and 15-pound rates and nearly equalled it at the 45-pound rate. Precipitation records assist materially in understanding the rapid change in status affecting borax and Colemanite. During the first month of the experiment there were only three light rains. In distribution and amount these appear to have been favorable to the dissolution and temporary retention of borax, favoring rapid uptake of boron

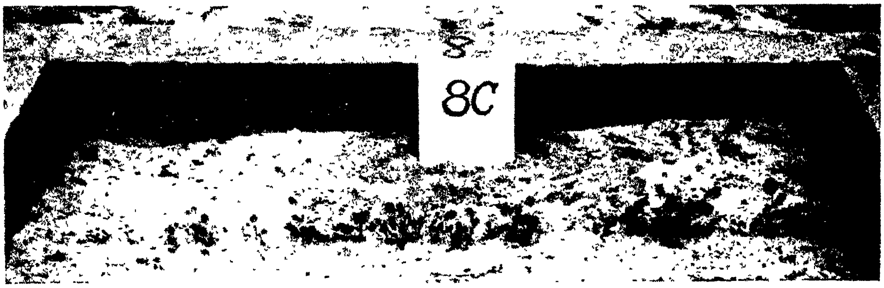

FIG. 1. EXTREME TOXICITY TO COLLARD SEEDLINGS FROM 45 POUNDS OF BORAX PER ACRE
Compare with figure 2

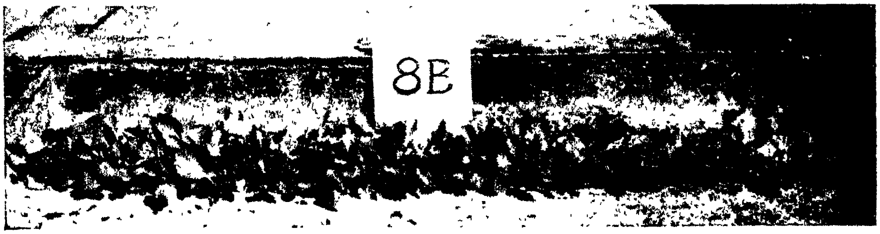

FIG. 2. COLEMANITE AT 45 POUNDS PER ACRE PRODUCED NO INITIAL INJURY

from that source. Then after the first samples were taken, for a period from January 29 to February 11, almost daily rain totaled 5.54 inches. These rains leached much of the borax to lower depths, but promoted the dissolution of Colemanite with attendant high rate of boron uptake, causing the crossing over of the curves (fig. 3) by the seventh or eighth week. Thus, it is concluded that the initial protection afforded by the use of Colemanite as a boron source can be expected to last for only a few weeks. The graphs show that the 100-mesh borosilicate furnished a small amount of boron initially, but gradually liberated a moderate and constant supply. In this respect it is most nearly comparable to the boron supplied natively under normal conditions for plant growth.

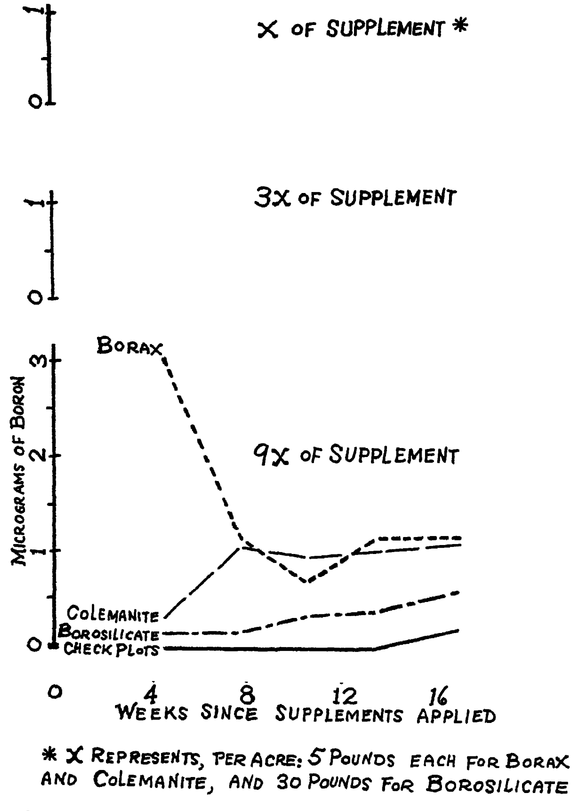

FIG. 3. BORON UPTAKE BY COLLARD FOLIAGE FROM SOURCES OF DIVERSE SOLUBILITY

As the collards grew, they were progressively thinned, finally to five per plot. The rutabagas were similarly thinned but left more closely spaced except where injury from borax had been severe and where in some instances, therefore, the stand was insufficient. There was considerable initial injury with even the 15-pound rate of borax, as shown by delayed emergence and some deformity in the seedlings. With Colemanite, although there was no initial injury, as the season advanced there was indication of unthriftiness, especially with rutabagas at the 45-pound rate. On May 5 the rutabagas were pulled, stripped of leaves, and weighed. The yields are given in table 3.

The severe deficiency symptoms in the rutabagas receiving no boron supplement are shown in roots 4 and 16 of figure 4. That the limiting factor was boron is demonstrated in B 14, which in addition to the elements supplied to Nos. 4 and 16 received boron as 5 pounds of Colemanite per acre. In all instances where Colemanite was used at the 5-pound rate there was complete freedom from internal abnormality. But where lime and the metallic minor elements were omitted, borax at the same rate produced a few roots showing watery-heart, the least severe form of the deficiency. On the other hand, borax at the next higher rates, 15 and 45 pounds per acre, gave some necrosis of fibrous roots and malformation of the main roots. In contrast to these conditions resulting from sensitivity to undersupply or oversupply of soluble boron, the results from

TABLE 3

Influence of boron sources of diverse solubility on yield of rutabagas grown in Lakeland fine sand

BORON SOURCE	YIELDS* AT VARIOUS RATES OF APPLICATION†		
	X	3X	9X
	gm.	*gm.*	*gm.*
Borax	473	436	313
Colemanite	681	396	311
Borosilicate	775	785	514

* Yields are in green weights of roots per treatment; mean of yields from check plots, 418 gm.

† On the basis of pounds per acre, the rate designated as "X" represents 5 pounds each for borax and colemanite, and 30 pounds for borosilicate.

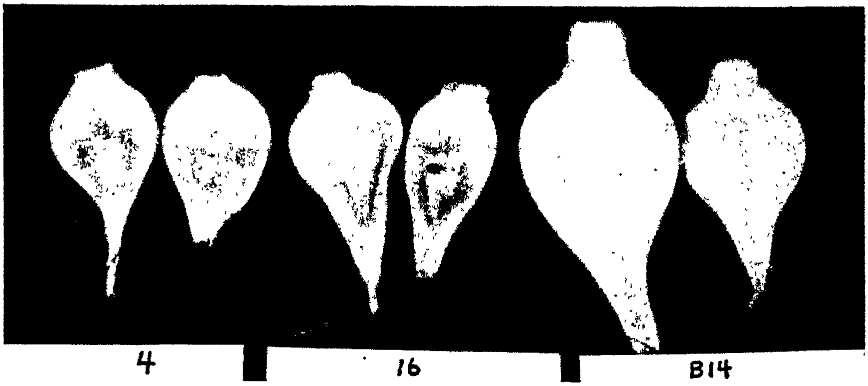

FIG. 4. EFFECTS OF COLEMANITE IN CORRECTING BORON DEFICIENCY OF RUTABAGAS

Roots reduced to approximately $\frac{3}{10}$ natural size. 4 received fertilizer plus lime; 16 received fertilizer plus copper, magnesium, manganese, and zinc; B 14 received 5 pounds of Colemanite per acre in addition to the elements furnished Nos. 4 and 16.

borosilicate impressively demonstrated the value of governed supply. In D 14 of figure 5 is shown the effect produced by the smallest amount, 30 pounds per acre. Although deficiency symptoms were eliminated, the texture was inferior to the roots from D 7, where the rate was 90 pounds per acre. The roots produced by this higher rate of borosilicate were remarkable for their internal and external texture and for their uniformity. The yield also was superior. At 270 pounds per acre, borosilicate caused the roots to become stringy and elongated (D 8, fig. 5), indicating that the optimum level for nutrient boron had been exceeded. Yet the yield in this case was not reduced to anywhere near the low level produced by 45 pounds per acre of either borax or Colemanite.

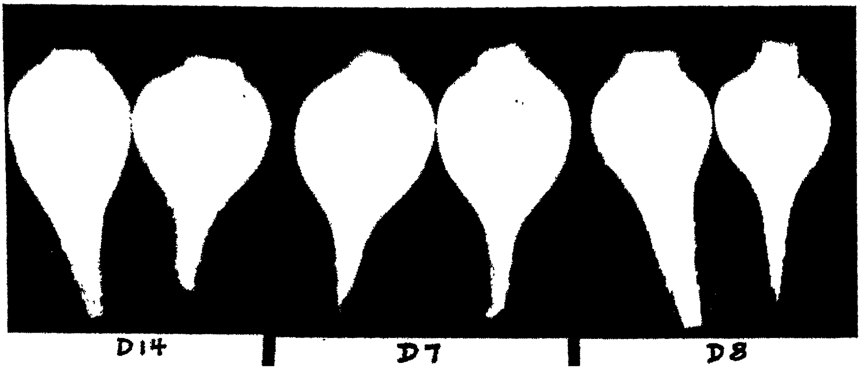

FIG. 5. EFFECTS OF BOROSILICATE ON QUALITY OF RUTABAGAS GROWN IN THE SAME BORON DEFICIENT SOIL WHICH PRODUCED ROOTS 4 AND 16 IN FIGURE 4

Roots reduced to approximately $\frac{3}{10}$ natural size. D 14 received same treatment as B 14, figure 4, except as the boron source it received 30 pounds of borosilicate per acre, which corrected boron-deficiency symptoms but produced slightly inferior texture; D 7 received same treatment as D 14, except borosilicate was applied at 90 pounds per acre, which resulted in unusually smooth internal and external textures, and ideal configuration; D 8 received same treatment as D 7 except for the rate of application of borosilicate, 270 pounds per acre—the roots were elongated and stringy, but no other symptoms of injury were noted.

DISCUSSION

Boron sources which because of their rapid solubility may be initially toxic to seedlings, yet leach to the point of insufficiency before the crop matures, would seem to be unsuitable for use in the study of minor element interactions. In many instances the true value of boron as a nutrient may have been obscured by use of these too-soluble materials, particularly in experiments evaluated solely by yield.

Of the domestic borates, it is believed that Colemanite will prove to be the most satisfactory as a supplement for sandy soils. It judicious use, both experimentally and practically, should be helpful in correcting boron deficiencies and in producing maximum yields. The commercial product, however, should be processed to remove impalpable material, as preliminary observations indicate that this portion of ground Colemanite acts similarly to borax in the soil and may prove equally toxic. Moreover, if Colemanite is mixed with superphosphate or with fertilizers containing large amounts of superphosphate, it may become undesirably soluble because of the action of the free sulfuric acid present. Borosilicate should be resistant to acids, and might, therefore, be a more satisfactory material for mixing with commercial fertilizers.

SUMMARY

Five boron sources covering a wide range of solubility were tested in the field on Lakeland fine sand.

Borax, fertilizer borate, Kernite, and Colemanite were used on the basis of 20 pounds borax-equivalent per acre. After 4 months and 21 inches of rain the boron remaining as boiling-water extractable in the 0–6 inch zone was, respectively, for the four materials: 3.5, 3.5, 7.1, and 10.6 per cent. Initially rapid dissolution of borax and fertilizer borate was reflected in depressed yields of both collards and rutabagas, though the same amount of boron as Kernite or Colemanite gave no detrimental effect.

The second unit represented an extreme range in solubility in that borax, Colemanite, and 20-mesh borosilicate were the sources. The first two were used at 10, 20, and 40 pounds per acre, and the borosilicate at 50, 100, and 200, and 400 pounds per acre. Their toxic effects upon hairy indigo (*Indigofera hirsuta* L.) were compared. Injury by borax at 40 pounds per acre was severe, and at 20 pounds moderate. Colemanite at the same rates gave no initial injury, but later produced marginal burn in the foliage. At the 40-pound rate the yield was reduced 78 per cent by borax, but only 25 per cent by Colemanite. Borosilicate produced no visible symptoms of injury, but the yield was reduced at the 200- and 400-pound rates of application.

The third unit employed borax and Colemanite at 5, 15, and 45 pounds, and 100-mesh borosilicate at 30, 90, and 270 pounds per acre. One month from seeding, foliage of the collards that had received borax as the supplement contained eight times more boron than where Colemanite was the source. After 3 more weeks and 5.54 inches of rain, boron in the foliage grown with Colemanite equalled or exceeded that in the foliage grown with borax. Colemanite produced no initial injury at either the 15- or 45-pound rates, whereas there was serious injury from borax at these rates; however, the final yield with Colemanite at these rates was depressed as much as with borax. Results with 5 pounds of Colemanite per acre were excellent, but borax at that rate was not equally effective in eliminating symptoms of boron deficiency. Borosilicate caused no toxicity: 30 pounds per acre eliminated all boron-deficiency symptoms in rutabagas; 90 pounds produced the best yield and the highest quality roots; 270 pounds caused the roots to become elongated and stringy, indicating that the optimum level for boron had been exceeded.

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BOOKS

Entwicklungslehre des Bodens. By WALTER L. KUBIËNA. Springer-Verlag, Wien, 1948. Pp. 215, figs. 5, plates 9. Price, paper-bound, $6.60; hard covers, $7.20.

The author previously published "Micropedology" (Collegiate Press, Ames Iowa, 1938) in English. The new book, dealing primarily with pedology, is in German. It is divided into four parts: theoretical basis of the science of soil evolution, character and basic laws, the systematic science, and the meaning of this science in relation to a natural system of soil classification. The system of soil classification is illustrated as an evolutionary tree, the two main branches of which represent underwater and semiland soils, and land soils. Eight smaller branches represent the soil classes, and still smaller branches the pedologic types. The book's apendix contains a glossary of pedologic terms, a list of 60 references, and nine plates, showing photographs of thin sections of soil under the microscope. The book should be of considerable interest to anyone concerned with soil classification.

HARVEY P. NEWTON.

Advances in Agronomy. Volume 1. Edited by A. G. NORMAN. Academic Press, Inc., New York, 1949. Pp. 439. Price $7.50.

This is the first of a series of annual reviews that are being published under the auspices of the American Society of Agronomy. This volume contains 10 papers prepared by 13 men who are especially well qualified to write on the subjects assigned to them. The papers deal with saline soils, new fertilizers, soybeans, clay minerals, alfalfa, soil microorganisms and plant roots, weed control, boron in soils and crops, potatoes, and phosphorus fixation. The central theme has been set at soil-plant relationships, which is the essence of agronomy. Judged by the first volume, this series is destined to fill an important need of agronomists. The successive volumes are certain to have a wide reading. The editor and his advisory board are to be congratulated on having made such a good start in this series of reviews.

Farm Structures. By H. J. BARRE AND L. L. SAMMET. John Wiley & Sons Co., Inc., New York, 1950. Pp. 650. Price $7.

The first of a series of text books on agricultural engineering sponsored by the Ferguson Foundation of Detroit, this book covers one of the six basic areas into which the field of agricultural engineering is divided by these authors; namely, farm structures, field power, field machinery, processing of farm products, farmstead power and equipment, and soil and water conservation. Its 29 chapters deal with materials, moisture, air, and temperature relationships, buildings for dairying, poultry, and crop storage, farm houses, costs, economic and efficiency aspects, stresses, beams, connections, and miscellaneous problems. The text is well illustrated. A list of references and a set of problems are appended to each chapter except the introductory one. The appendix contains a large number of very useful data for calculating requirements and estimating costs. An interesting table on the bearing values of soils is given in the text, and another on the time required for excavating earth, in the appendix. The book is well written and should prove to be a very useful teaching aid.

Forage Crops. By GILBERT H. AHLGREN. McGraw-Hill Book Company, Inc., New York, 1949. Pp. 418, figs. 99. Price $5.

This book is of special importance in that it deals with crop plants that are entitled to much more consideration in the classroom than has been given them. The author has endeavored to bring all the more important forage plants of the temperate zone together under one cover and to consider each of them in relation to the others in the farming program. Of the 37 chapters, 10 deal with the hay and pasture legumes, including kudzu; 8 are concerned with the more common grasses, including the cereal hay crops; and the rest are designed to cover seeds, seedbed preparation, cultivation, harvesting, silage-making, and related subjects. This volume is entitled to a prominent place on the agronomist's book shelf and should be of considerable interest to other persons who have to do with the many phases of general agricultural production.

Introduction to the Theory of Probability and Statistics. By NIELS ARLEY AND K. RANDER BUCH. John Wiley & Sons, Inc., New York, 1950. Pp. 236, figs. 21. Price $4.

This is one of Wileys' "Applied Mathematics Series" of books which deal with the theories that underlie the physical and biological sciences and with the mathematical techniques that are needed for solving problems in these sciences. The original book appeared in Danish in 1946, and this is the first English edition. The first three chapters have to do with elementary principles. The remainder of the book considers random variables, mean values and dispersion, normal distribution, limit theorems, practical importance of theory of probability and its application to statistics, theory of errors, and theory of adjustment. The appendix contains a discussion of factorial n and the matrix theory, five tables of distribution, a set of 90 problems, and three pages of references. The book assumes a knowledge of calculus and of linear equations, and is of considerable importance to those who have the necessary mathematical background.

Isotopes. United States Atomic Energy Commission. U. S. Government Printing Office, 1949. Pp. 201. Price, paper cover, $0.45.

Primarily a 3-year summary of the distribution of radioisotopes, this brochure also deals with the production of isotopes, their use in the United States and abroad, training in isotope techniques, and the future of the program. The appendix gives statistical information on the growth of the program, an outline of the procedure for obtaining isotopes, a list of those available for use, and a bibliography of papers published or in preparation by some 2,000 workers in this field of research. The bibliography is presented under the headings medicine, animal physiology, bacteriology, plant physiology, physics, chemistry, industrial research, and general.

Selenium. By SAM F. TRELEASE AND ORVILLE A. BEATH. Published by the authors, Columbia University, New York. Pp. 292. Price $5.50.

Selenium poisoning is a serious menace to livestock in the vast grazing areas of our western states. This book deals with the problem in detail. The first chapter has to do with the history of the selenium problem, and the remaining seven chapters cover the distribution of selenium in rocks and soils, its accumulation in plants, its poisonous effects on animals, its relation to public health, prevention and control of selenium poisoning, and chemistry of the element. The bibliography contains more than 300 references. This is a highly important book that merits study not only by those who are concerned with livestock production in the affected area but by those who are dealing with the somewhat similar problem of molybdenum poisoning. It is conceivable that molybdenum is an additional contributing factor to the troubles in that region. The book should also be of much interest to those who are concerned with minor elements and problems related thereto.

Socialized Agriculture of the USSR. By NAUM JASNY. Stanford University Press, California, 1949. Pp. 837. Price $7.50.

The author of this book lived in Russia until after the Bolshevik Revolution, was an associate member of the Supreme Food Council and one of the advisers of the Supreme Economic Council under the Kerensky regime, and later served as a grain expert in trade representations in Germany. He dedicates the book "to those in Soviet Russia—far away and yet so near—who believe in science, unadorned and unadulterated science; statistics, simply factual statistics; plain truth, untarnished and unvarnished." One need read only a few pages to become aware that agricultural conditions in Russia are so foreign to our ideas and ideals as to greatly emphasize the relatively high income and opportunity of American farmers. The author discusses socialized farming in all its details and shows clearly that the peasant is merely a slave of the state. Neither the mineral nor the agricultural resources of Russia are large in proportion to the more than 170 million people in that country, and there is a little evidence that collectivization in agriculture has produced either "abundantly or cheaply." The author had considerable difficulty in separating fact from fancy, but he has succeeded in piecing together what would appear to be a dependable account of U.S.S.R. accomplishments. The four full-page figures of the principal political divisions, natural divisions, average annual precipitation, and soils of the U.S.S.R. are of special interest. The book fills a very important need.

Soil Science Society of America Proceedings, 1948. L. G. MONTHEY Secretary-Treasurer, Madison, Wisconsin. Pp. 587. Price $7.50.

This is volume 13 of these Proceedings and contains more than 100 papers that were presented at the annual meeting of the Society at Fort Collins, Colorado, August 24 to 27, 1948. These papers were given under six sections entitled "Soil Physics," "Soil Chemistry," "Soil Microbiology," "Soil Fertility," "Soil Genesis, Morphology and Cartography," and "Soil Technology." In addition, there were two general papers, one by T. M. Bushnell on "Japan's Dilemma," and the other by B. J. Birdsall on "Technical Collaboration in Agriculture in the Western Hemisphere." The appendix contains the minutes of the meeting and reports of committees on chemical analyses, terminology, policy, roadside soil-type markers, and physical analyses. Also appended are a report of representatives of the Society on the Division of Biology and Agriculture of the National Research Council and a statement offering suggestions on the preparation of slides and use of projection equipment. Every soil scientist will want a copy of this volume close at hand for ready reference.

THE EDITORS.

BIOLOGICAL OXIDATION OF MANGANESE IN SOILS

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Development of "gray speck" in oats and "marsh-spot" in peas is due to manganese deficiency and can be cured by applying manganous sulfate to the soil. The initial transformation of the manganous ion in soils of pH 5.8–8.9 is its oxidation (3, 4). Various workers (1, 2, 3, 6, 7) have shown that oxidation of manganese in soils can be brought about by biological agencies.

An investigation of the microorganisms responsible for this oxidation and of the nature of the process by which the microorganisms oxidize the manganese is described in this paper.

ISOLATION OF SOIL MICROORGANISMS CAPABLE OF OXIDIZING MANGANESE

Gerretsen (2) demonstrated the biological oxidation of manganese in soils by mixing 30 gm. of soil with 25 ml. of water and 100 ml. of 2 per cent agar at 40°C. in a petri dish 11 cm. in diameter. When the mass was solid, a hole 2.5 cm. in diameter was cut from the center, and agar containing 1 per cent $MnSO_4$. usually mixed with sand, was poured into the gap. The dish was then incubated at 25°C. and the development of brown deposits of manganese oxide observed during the following days.

Leeper and Swaby (3) modified Gerretsen's method by reducing the quantities of soil and agar and incubating at 27°C. Their directions were followed for the preparation of enrichment plates for the isolation of manganese-oxidizing microorganisms (fig. 1). The plates were incubated at 22°C.

Enrichment plates were prepared with deficient soils that could not be permanently cured by addition of manganous sulfate. It was thought that if specific manganese-oxidizing organisms were responsible they would be in these soils Of the soils used for enrichment plates, only the Penola and University (3) were used for isolations, as the development of the oxide deposits in the other soils was poor.

Media used for isolation

Of the media that have been used for isolation purposes by other workers those of Gerretsen (2) and of Beijerinck (1) were employed in the investigation

Gerretsen's medium—calcium citrate, 2 per cent; $MnSO_4 \cdot 4H_2O$, 0.5 per cent; $(NH_4)_2SO_4$ 0.2 per cent; NH_4MgPO_4, 0.001 per cent; agar, 2 per cent; tap water; adjusted to pH 6.0 and autoclaved at 15 pounds for 20 minutes.

Beijerinck's medium— $MnCO_3$, 1.0 per cent; K_2HPO_4, 0.05 per cent; NH_4Cl, 0.05 per cent agar, 2.0 per cent; tap water; autoclaved at 15 pounds for 20 minutes; pH 7.0.

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[1] The authors wish to thank Associate Professor Ethel McLennan for her assistance in identifying the fungi.

Since investigation indicated that neither of these media was satisfactory, the following medium was developed and subsequently employed for most of the work:

Soil-manganese agar—sterile soil, 100 gm.; tap water, 400 ml.; agar, 8 gm.; $MnSO_4 \cdot 4H_2O$, 0.025 gm.

The soil, a moist sandy loam of pH 6.8, was autoclaved in a glass jar with a screw top for 7 consecutive days at 15 pounds for 20 minutes. The water, agar, and manganous sulfate were then added and melted, and the medium was tubed and reautoclaved ready for use.

Isolation on Gerretsen's medium

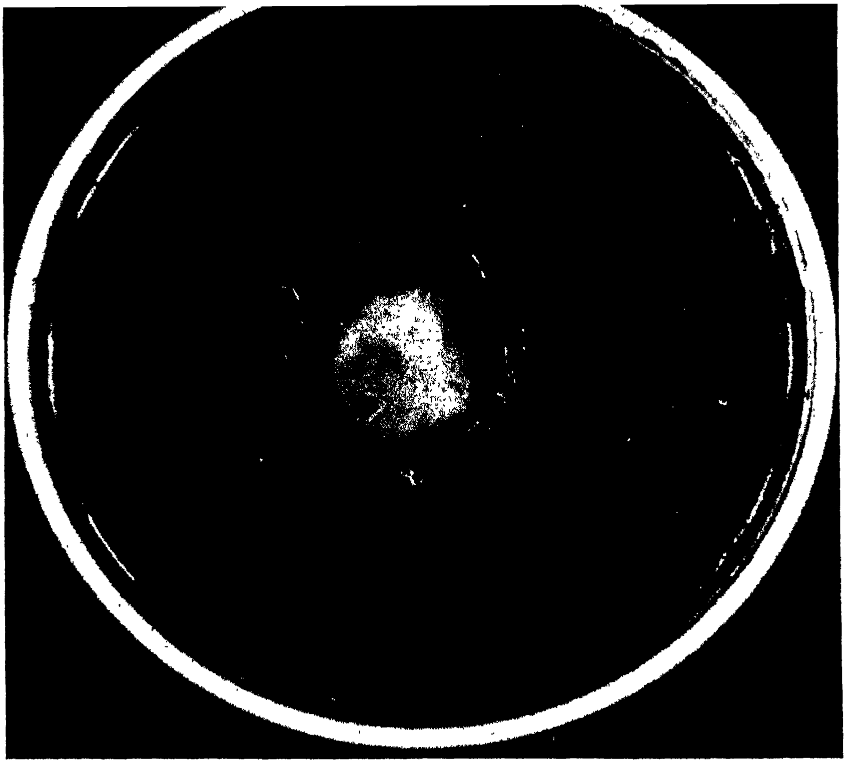
Brown-black specks in the deposits of manganese oxide in the enrichment plates were picked out and emulsified in sterile tap water and then plated by the dilution streak technique on Gerretsen's solid medium and incubated at 22°C. After 4 days, brown colonies developed on the plate, and the agar turned light brown where there were large numbers of colonies (fig. 2). The brown colonies on these plates were selected on the basis of macroscopical differences and replated on fresh medium to obtain pure cultures. Among those obtained which could cause the oxidation of manganous sulfate in this medium were organisms belonging to the genera *Bacillus*, *Corynebacterium*, *Aerobacter*, *Pseudomonas*, and *Proteus*.

So far as can be ascertained, Gerretsen made no attempt to reproduce the oxide rings with organisms isolated on his medium. To determine, therefore, whether these organisms were responsible for the production of the oxide rings in the original soil plates, washed suspensions were inoculated into sterile soil agar (fig. 1). The sterile soil used was at pH 6.8, as Gerretsen and Leeper and Swaby found that biological oxidation was greatest at pH values near 7. The soil was sterilized by autoclaving at 15 pounds for 20 minutes on 7 consecutive days. The sterile soil was mixed with water and agar to give a soil suspension in 2 per cent agar and reautoclaved. Pure cultures of isolates on Gerretsen's medium were grown on meat infusion agar slopes and when there was abundant growth (24 hours at 22°C.) the cultures were emulsified in sterile tap water and centrifuged, the supernatant was poured off, and the bacteria were resuspended in sterile tap water (4 to 5 ml.). Sterile soil agars (20 ml.) at 40°C. were inoculated with these suspensions, and when solid, a central core of manganous sulfate agar was inserted into each plate. The sterile soil agar was inoculated with pure and mixed suspensions of *Bacillus* sp., *Pseudomonas* sp., *Corynebacterium* sp. Additional plates were prepared with sterile soil agar containing 0.001 per cent calcium citrate to see whether the deposition of oxide by these organisms was accelerated by the presence of citrate. The plates were incubated at 22°C.

No oxide rings appeared in any of the plates. In the presence of citrate, however, a positive reaction of manganic oxide was obtained with the benzidine reagent (1 per cent benzidine hydrochloride in 2 *N* acetic acid) in plates inocu-

FIG. 1. UNIVERSITY SOIL AGAR PLATES pH 6.8 (ABOVE) AND 7 (BELOW) AFTER INCUBATION WITH $MnSO_4$ AGAR IN CENTRAL PLUG

Note ring deposit of manganese oxide.



lated with organisms, the blue color extending into the central agar core. All the soil agar plates and the control citrate soil agar yielded negative tests.

As a matter of interest an attempt was made to demonstrate the oxidation of manganese by these organisms in the presence of a citrate-producing mold, *Aspergillus niger*.

One series of sterile soil agar plates was inoculated with spores of *A. niger* and one series with *A. niger* and a washed suspension of a *Corynebacterium* that brought about active oxidation on Gerretsen's medium. The plates were incubated at 22°C. for 18 days and tested for oxidized manganese with the benzidine reagent. A positive reaction was recorded only with the association.

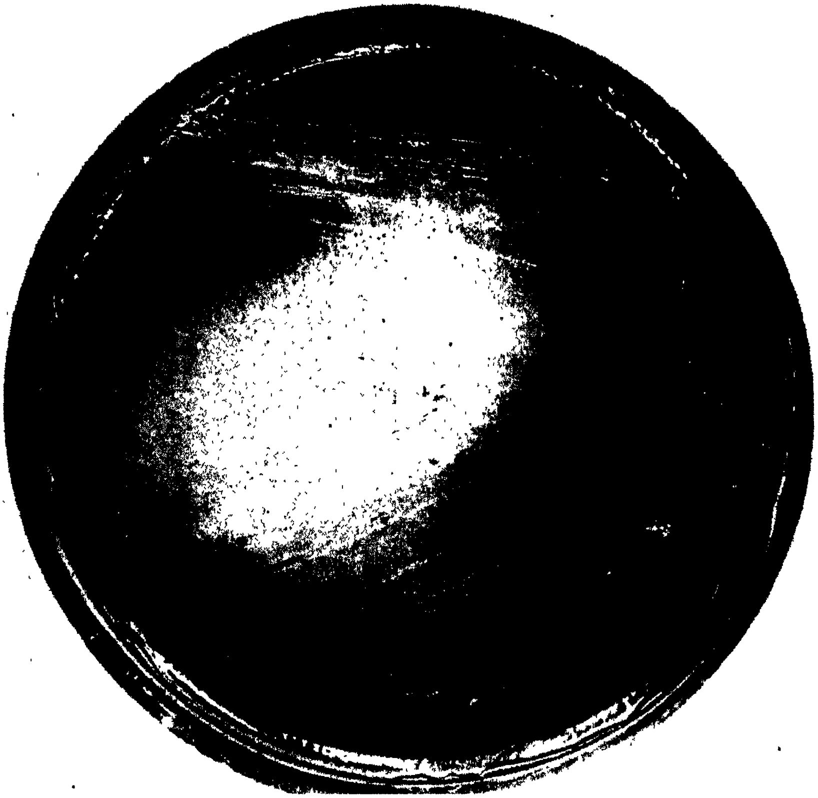


FIG. 2. GERRETSEN'S MEDIUM INOCULATED WITH BROWN RING MATERIAL AND FLOODED WITH BENZIDINE HYDROCHLORIDE AFTER 7 DAYS AT 22°C.

Note staining of colonies and also of the surrounding medium.

Söhngen (8) found that oxidation of manganese was promoted by the presence of hydroxyacids. Jones[2] has shown that the rate of nonbiological oxidation of manganese in the presence of citrate increased with increase of pH. This suggested that the oxidation of the manganese on Gerretsen's medium was initiated by a rise in pH in the presence of citrate. The following experiment was therefore conducted to see whether the organisms which turned brown on Gerretsen's medium could raise the pH of the medium.

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[2] Jones, L. H. P. The oxides of manganese and their relation to the availability of manganese to plants in soils. 1949. [Unpublished Ph.D. thesis. Copy on file Univ. Melbourne.]

Sterile liquid Gerretsen's medium was prepared and the pH adjusted to 5.8. This pH was used to reduce nonbiological oxidation in the controls and also to determine whether the bacteria could grow at this pH. Leeper and Swaby (3) found that the lowest pH of soil which still formed deposits of manganese oxide was 5.8.

The medium was tubed in 15-ml. amounts in 6- by ¾-inch tubes, autoclaved, and inoculated with species of the following organisms: *Corynebacterium*, *Pseudomonas*, *Aerobacter*, *Bacillus*, and *Proteus*. After 12 days at 22°C., the pH values of the cultures were determined with a glass electrode and the tubes tested for oxidized manganese. Results are shown in table 1.

TABLE 1

pH of cultures of organisms in liquid Gerretsen's medium after 12 days at 22°C.

	pH	Mn^{+++} TEST—BENZIDINE
Corynebacterium	7.60	Blue ring and blue sediment
Pseudomonas I	7.75	Blue ring and blue sediment
Proteus	7.60	Blue ring only
Pseudomonas II	7.62	Blue ring only
Aerobacter aerogenes	7.60	Blue ring only
Bacillus	6.00	Solution turns green-yellow-orange
Control		Solution turns pale blue, fades

Oxidized manganese was detected in all the tubes including the controls. In tubes inoculated with the organisms (except *Bacillus* sp.), a ring which stained blue with benzidine hydrochloride was formed. The ring is probably due to oxidized manganese on the bacterial cells which tend to grow near the liquid-air interface. Growth of the *Bacillus* sp. was very poor.

From the pH determinations it appears that the more rapid oxidation could be due to an increase in pH (1.8 units) produced by the bacteria. On an agar plate, aeration is optimal for oxidation, and the pH in and around the colony could quite conceivably be higher than that recorded in the liquid medium and the effect of both these could result in the deposition of oxide in the colony.

An additional suggestion for increased oxidation in Gerretsen's medium in the presence of organisms is that they produce some organic compound from citrate which is more efficient than citrate in causing oxidization of manganese.

Gerretsen's medium selects organisms that favor in some way, such as by increasing pH, the nonbiological oxidation of manganese in the presence of hydroxyacids and does not select, as thought by Gerretsen and by MacLachlan (5), organisms that are responsible for formation of the oxide ring in the soil.

Studies made on the biological oxidation of Mn and its relationship to Mn deficiency in oats, in which the observations were based on counts of manganese oxidizers obtained by use of this medium, are therefore misleading.

Isolation on Beijerinck's medium

The same technique for isolation was used on Beijerinck's medium as on Gerretsen's medium, but no brown colonies appeared during 14 days' incubation. Beijerinck's enrichment method (1), in which the manganous carbonate agar plates are sprinkled with soil and incubated at 22°C., was then used. After 14 days, a few light brown zones of manganese oxide appeared. It was found that freshly prepared and washed manganous carbonate was unstable when moist, and oxidized manganese could be detected after 12 hours with benzidine hydrochloride. Further attempts to isolate on Beijerinck's agar medium were discontinued.

Isolates from Gerretsen's medium could not oxidize the manganese in Beijerinck's medium. Beijerinck demonstrated the oxidation of manganous carbonate by dusting filter paper with manganous carbonate and wetting it with a sterile solution of 0.1 per cent ammonium chloride and 0.1 per cent potassium phosphate in tap water. The filter paper was then sprinkled with soil and incubated in a petri dish at 22°C. This experiment was modified by replacing the manganous carbonate with a 0.05 per cent solution of manganous sulfate at pH 6.8. Filter papers wetted with this second solution were inoculated with soil and brown ring material. No manganese oxide developed on the filter paper during 25 days.

Experiments with soil manganese agar

As Beijerinck's medium was undesirable, an attempt was made to prepare a medium in which the manganous ion was stable but could be specifically oxidized by the manganese-oxidizing organisms from the soil.

Moist sandy loam at pH 6.8 was autoclaved at 15 pounds for 20 minutes on 7 consecutive days. A 5 per cent suspension of sterile soil in tap water was prepared, and after the sand fraction had settled, the supernatant was made up with agar to give a 2 per cent soil agar. This was tubed and autoclaved at 15 pounds for 20 minutes.

Plates of sterile soil agar with a central manganous sulfate agar plug were prepared and inoculated with an emulsion of the material from the brown ring deposits described above. To avoid toxic concentrations of manganous ion (3) in the soil agar and to dilute the inoculum, the inoculum was plated radially from the center of the plate and continuously around the plug. These plates and uninoculated plates were incubated at 22°C. for 10 days. A small number of dark brown colonies appeared on the inoculated plates, and these colonies gave positive tests for manganese oxide with benzidine hydrochloride; the uninoculated plate gave negative tests.

As the method for preparing the plates described above was tedious, a soil manganese agar was prepared containing various amounts of manganous sulfate and inoculated with the brown colonies from the above plates. For the soil used, concentrations of $MnSO_4 \cdot 4H_2O$ in the medium above 0.25 per cent prevented oxidation but not growth during 3 weeks. The concentration of $MnSO_4 \cdot 4H_2O$ adopted for the *soil manganese agar* was 0.005 per cent by weight of medium. The brown growth from the initial plates was plated on this soil Mn agar in an attempt to isolate pure cultures of the oxidizing organisms. After 3 days at 22°C., brown colonies, which were fairly well isolated, were picked off and replated. Brown colonies developed where the plate was first streaked, but in the dilution zone single colonies were never brown (fig. 3). Sometimes where two colonies were close together or where one was surrounded by another, one colony was uniformly dark brown or had a brown ring around its margin. These brown colonies turn dark blue with benzidine hydrochloride. Single colonies with different macroscopical characters were picked off these plates and plated on soil manganese agar. None of these turned brown during 10 days at 22°C. These

FIG. 3. SOIL-MANGANESE AGAR MEDIUM INOCULATED WITH BROWN GROWTH ISOLATED FROM OXIDE DEPOSIT

Note brown colonies in primary inoculation zone and white colonies in dilution zone.

observations led to the belief that oxidation of the manganese may be due to an association of two or more organisms.

Pure cultures isolated from the soil manganese agar were therefore mixed in pairs on the soil manganese agar to see whether oxidation would occur. Certain pairs of organisms produced brown growth after 3 to 4 days. This growth stained blue with benzidine hydrochloride.

The organisms in these pairs belong to the genera *Corynebacterium*, *Flavobacterium* (two strains), and *Chromobacterium* (two strains). The *Corynebacterium* was common to all pairs. The oxidizing pairs also oxidized the manganese on a soil water extract manganese agar.

This medium was prepared by shaking a 5 per cent suspension of sterile soil and water for 30 minutes, allowing it to settle for 24 hours, and then syphoning off the supernatant. The supernatant was then clarified through a No. 6 Ekwip filter pad. The pH was adjusted to about 6.5 and then 0.005 per cent by weight of manganous sulfate and 2 per cent agar were added. The solution was then autoclaved at 15 pounds for 20 minutes.

No oxidation took place on three chemically defined media of the following composition, in the preparation of which use of sugars and of hydroxy acids, such as citrates and tartrates, was avoided:

	per cent
1. $MnSO_4 \cdot 4H_2O$	0.005
NH_4NO_3	0.5
K_2HPO_4	0.001
Agar	2
Tap water	
pH 6.5	

	per cent
2. Peptone	0.01
$MnSO_4 \cdot 4H_2O$	0.005
K_2HPO_4	0.001
Agar	2
Tap water	
pH 6.5	

3. Sodium glycerophosphate	0.5
$MnSO_4 \cdot 4H_2O$	0.005
NH_4NO_3	0.5
Agar	2
Tap water	
pH 6.5	

Reproduction of oxide ring with paired organisms

An attempt to reform the ring deposit of oxide in sterile soil at pH 6.8 with the oxidizing pairs was made by the method described earlier. After 3 days, ring deposits occurred in all plates. A mixture of the *Corynebacterium* and one of the *Chromobacterium* strains gave the best deposit (fig. 4). The similarity between the natural deposit (fig. 1) and artificially produced rings leaves little doubt that these organisms are responsible for the oxidation of manganese in the plates of University soil at pH 6.8.

Oxidation of manganese by fungi

An attempt was made to isolate manganese-oxidizing organisms by directly depositing small lumps from soil on the surface of the soil water extract agar and the three chemically defined media. Brown manganic oxide stains appeared in the media under the lumps, and when this stained material was plated on all four media, oxidation was noticed only on the soil water extract medium. This oxidation appeared to be due largely to fungi, as the stains consisted of a large number of brown macroscopic spherites and thick brown hyphae. From these brown stain areas, three fungi were isolated which could oxidize manganese in the soil water extract Mn agar when they were in pure cultures. They belonged to the genera *Cladosporium*, *Tringschemia* (an Ascomycete), and *Pleospora* Rabb.

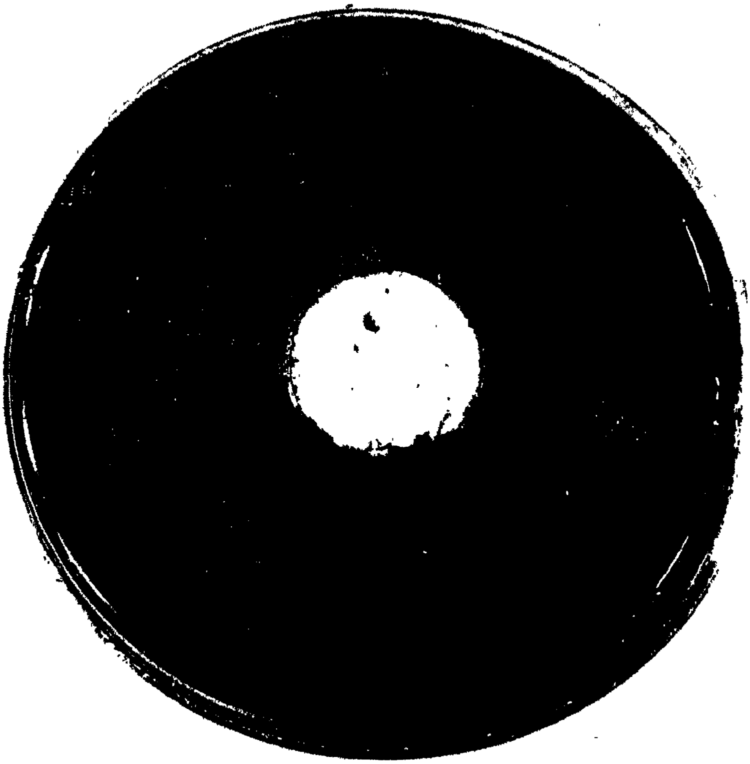

FIG. 4. STERILE SOIL AGAR INOCULATED WITH *Corynebacterium* AND *Chromobacterium* AFTER INCUBATION WITH $MnSO_4$ AGAR IN CENTRAL PLUG

Note ring deposit of manganese oxide; compare with figure 1.

With *Cladosporium* sp., oxidation occurs almost all over the colony, as it spreads slowly. The oxide is deposited in the form of a sheath around the hyphae. At the tips of the hyphae small irregularly arranged masses of oxide are deposited.

With *Tringschemia* sp., oxidation occurs only in the area around the point of inoculation. The fungus is a rapid spreader. The oxide is deposited to form a sheath along some hyphae and is also deposited in small masses a short distance from the hyphae.

With *Pleospora* Rabb., there is a large area of oxidation but it does not extend to the outer zone of the colony. The oxide is arranged irregularly along the hyphae as small spherical masses, many of which are at some distance from the hyphae.

It is suggested that these and probably other fungi may be responsible for the formation of the brown-black spot deposits of oxide in the acid soils (fig. 5).

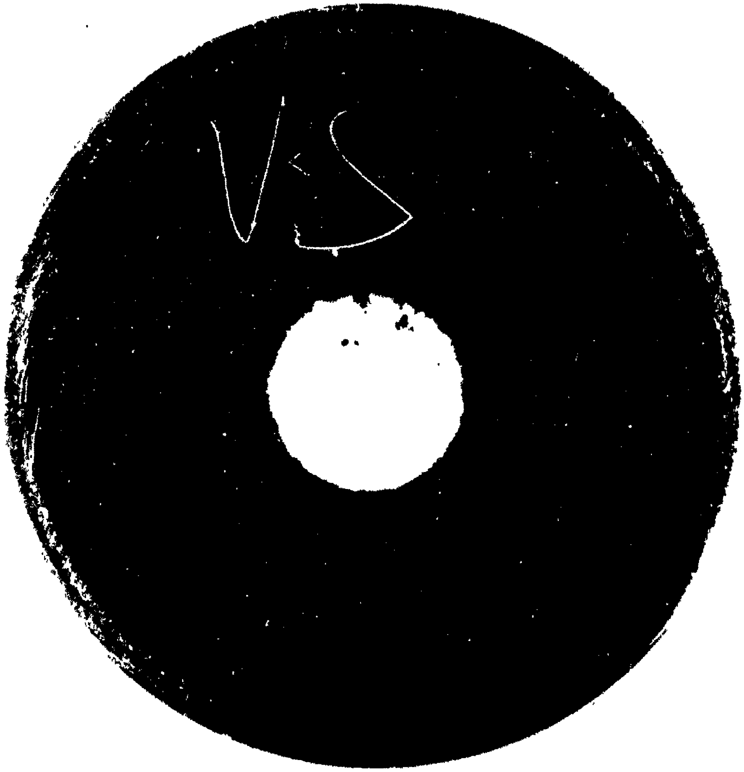

FIG. 5. UNIVERSITY SOIL AGAR PLATE AT pH 5.8
Note black spots of manganese oxide at random on the reverse side of the dish.

OBSERVATIONS ON ASSOCIATIVE ACTION OF OXIDIZING BACTERIA

Behavior of the organisms on Gerretsen's medium

The five species concerned in the associative oxidation of manganese were inoculated on Gerretsen's manganese citrate medium and incubated at 22°C. Rapid oxidation was produced by the *Corynebacterium* but none by the chromogenic gram-negative rods. This finding suggested the possibility that other organisms oxidizing manganese on Gerretsen's medium might replace the *Corynebacterium* in the mixtures. This, however, was not the case.

pH changes

Measurements were made of pH changes in various parts of the agar following the oxidation of manganese by organisms in the unsterilized soil agar. The results, shown diagrammatically in figure 6, indicate that in the zone of oxidation the pH had fallen 0.34 of a unit.

Determinations of pH were also made on sterile University soil manganese agar plates inoculated with washed suspensions of *Corynebacterium* and *Chromobacterium*. The uninoculated plates remained at pH 6.80 after 9 days at 22°C., but the inoculated plates had risen to pH 8.12, an increase of 1.32 units.

It is considered that the manganese-oxidizing organisms tend to cause a pH rise in the soil during their metabolism and that the pH determination of the various zones in the unsterilized University soil plate gives the pH resulting from the combined activities of the whole soil flora.

Obviously, the oxidation of manganese brought about by the pairs is not due simply to a pH effect. It seems apparent that some metabolic by-product of one organism is used by the other in the oxidation of manganese. Only preliminary observations of an inconclusive nature have been made on this aspect, and they seem to indicate the probability that the *Chromobacterium* produces a heat-labile or volatile substance which is used by the *Corynebacterium* in the oxidation of the manganese.

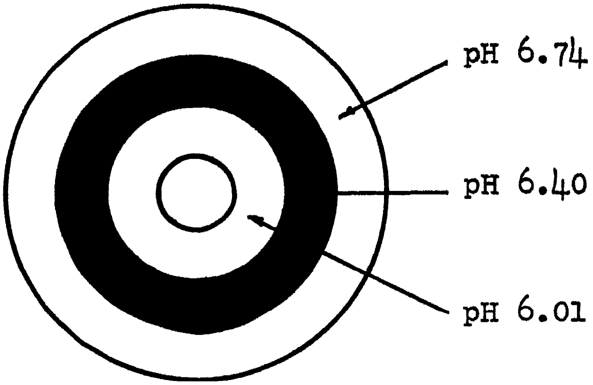

FIG. 6. pH VALUES OF ZONES IN A SOIL PLATE AFTER 9 DAYS AT 22°C.

SUMMARY

Organisms of the type isolated by Gerretsen were isolated on his medium but were found to be incapable of reproducing the phenomenon for which he considered them responsible, namely, the oxidation of manganese in unsterilized soil. The oxidation observed on a citrate medium is apparently due to a non-biological oxidation of the manganese in the presence of oxyacids at high pH values: the organisms need only render the medium alkaline to achieve this.

By use of a soil extract agar, it was possible to demonstrate that oxidation in certain soils was due to the associative action between two organisms, one a

Corynebacterium and one a pigmented member of the genus *Chromobacterium* or *Flavobacterium*. The oxidation is not a simple pH effect.

Certain fungi of the genera *Cladosporium*, *Trirgschemia*, and *Pleospora* were found which readily oxidized manganese and are probably important in acid soils.

The existence of the associative action between two organisms makes it practically impossible to assess the numbers of manganese-oxidizing organisms in the soil. The finding that organisms isolated on Gerretsen medium were unable to oxidize manganese in sterilized soil casts doubt on the significance of previous reports on counts of manganese oxidizers.

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ZINC RELATIONSHIPS IN AIKEN CLAY LOAM

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It has been known for many years that some soils fix zinc in a form not readily available to plants. This has necessitated use of zinc sprays in correcting deficiencies of this element in soils.

Chandler, Hoagland, and Hibbard (2) found, when they mixed soil with a known amount of zinc sulfate and subsequently filtered and analyzed the filtrate for zinc, that the fixing power ranged from 170 to more than 1,000 ppm. for the several soil samples being studied. This zinc retained by the soil should be, in part at least, available to plants, since it represents exchangeable and adsorbed, as well as fixed, forms of zinc. It could also include any zinc precipitated as an insoluble compound at the particular pH of the soil solution.

Peech (9) in studying the availability of ions in sandy soils found that zinc applied to soil could virtually all be extracted with *N* NaCl solution at a pH of 3.0. As the pH of the soil was increased, the amount of zinc extractable diminished; practically all the zinc was fixed at pH 8.0. His findings also reveal that when 300 pounds of zinc per acre was applied to Norfolk fine sand at a pH of 6.0, approximately 150 pounds (0.23 me. per 100 gm.) was fixed.

More recently, Elgabaly and Jenny (4), in studying the exchange mechanism of zinc montmorillonite clays, found that most of the zinc was replaced with neutral normal ammonium acetate solution but a few milliequivalents per 100 gm. of clay were irreversibly fixed. Hydrochloric acid at four times symmetry only replaced some 70 per cent of the zinc, exchangeable with ammonium acetate, from a zinc montmorillonite.

Further investigations of Elgabaly, Jenny, and Overstreet (3) showed that barley roots could readily utilize zinc ions adsorbed on clay particles.

When zinc salts are applied to soils as fertilizer, it would seem that at least a considerable portion should be available to plants. This, however, is apparently not always true in practice.

The present paper is concerned with adsorption, exchange, and fixation of zinc by Aiken clay loam. This soil has been reported to contain essentially kaolinitic clay minerals (7).

SORPTION OF ZINC BY SOIL TYPES

Air-dry samples of soil, usually 10 gm., were shaken on a mechanical shaker with 100 ml. of approximately 0.01 *M* $ZnSO_4$ solution. At definite time intervals, duplicate samples were removed from the shaker and filtered. The filtrates so obtained were analyzed for zinc by the ferrocyanide titration method (8). The decrease in zinc content of the zinc sulfate solution after being in contact with the soil was taken as the amount fixed or adsorbed by the soil.

The results expressed as milliequivalents of zinc sorbed per 100 gm. of soil are shown in figure 1. The equivalent weight of zinc is taken as 32.69. Aiken appears to be markedly different from the other soils. Vina loam and Hanford very fine sandy loam show a slight tendency toward a sorption curve similar to Aiken; Yolo silt loam and Corning gravelly loam show less tendency to be similar to Aiken.

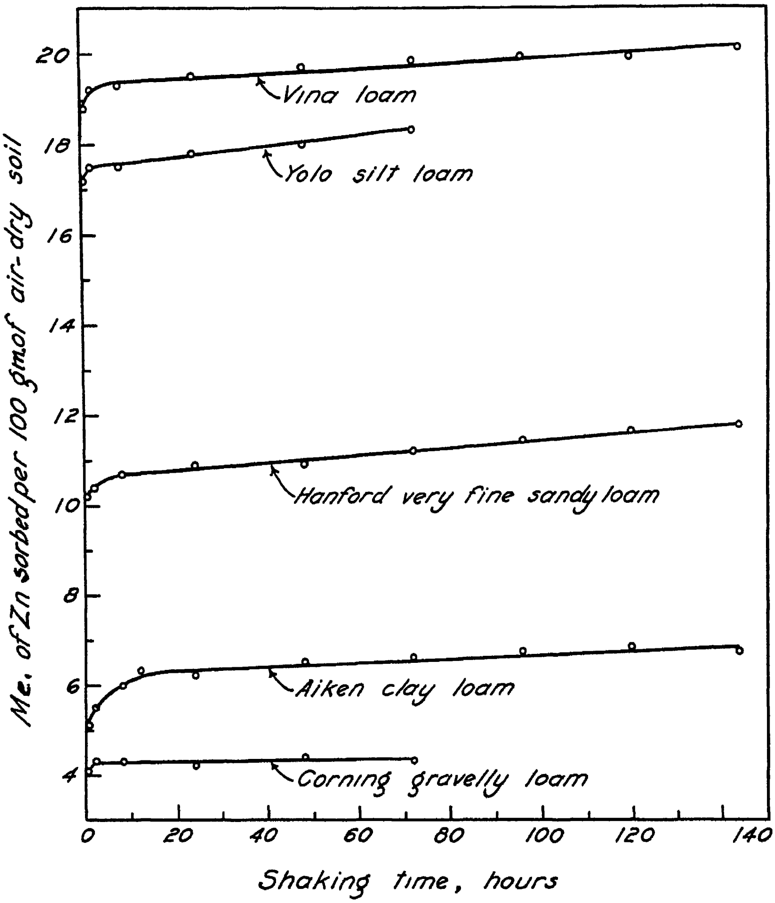

FIG. 1. SORPTION OF ZINC BY SEVERAL SOIL TYPES

It has been fairly well established that exchange reactions are very rapid, equilibrium being reached in a matter of seconds. Thus, a curve such as that obtained with Aiken clay loam suggests the possibility that factors other than simple exchange are involved in the sorption of zinc by this soil.

The differences in amounts of zinc retained by the various soils are to be expected. The exchange capacities vary so that Vina loam with the highest exchange capacity (29 me.) retains the most zinc. The organic matter content and the pH of the soil will both affect the sorption of zinc. Jamison (5) found that zinc was more soluble at the lower pH values, especially below 5.0. The Yolo and Hanford soils are approximately neutral in reaction, whereas Vina has a pH of 6.6, Corning 5.9, and Aiken 5.3. Then, too, some cations are more readily replaced by zinc than others; consequently the cations present in the soil will affect the sorption of zinc.

To determine relative effect of various cations on the sorption of zinc, Na-Ca-, H-, and K- homionic Aiken soils were prepared by leaching with solutions of the appropriate chlorides, and Mg- soil was prepared by leaching with the sulfate. Excess salts were removed with 95 per cent ethyl alcohol, and finally the soils were dried. Ten-gram samples were shaken for 24 hours with 0.01 *M* $ZnSO_4$ solution, and zinc was determined in the filtered extract. It was found that Na-, Ca-, K-, Mg-, and H-Aiken soils sorbed 8.44, 7.56, 7.45, 6.98, and 3.76 me. of zinc per 100 gm. of air-dry soil, respectively.

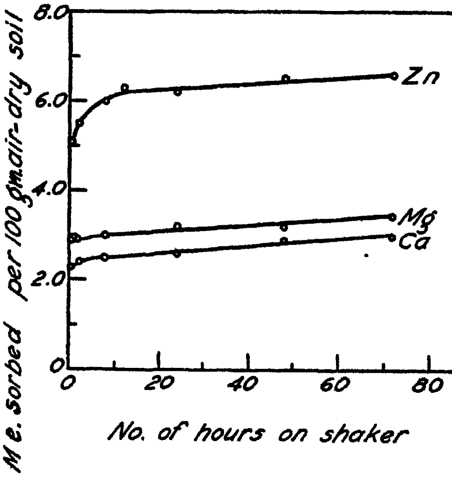

FIG. 2. SORPTION OF CALCIUM, MAGNESIUM, AND ZINC BY AIKEN CLAY LOAM

At least two questions presented themselves concerning the zinc sorption curve for Aiken clay loam:

1. Is zinc different from other divalent cations such as Ca^{++} and Mg^{++}?
2. Aiken clay loam is very well aggregated and, thus, does not disperse readily. Is it possible that, as shaking continued, dispersion became more complete and hence more surface area exposed? This might then provide a greater number of exchange positions and account for the increasing sorption of zinc.

To attempt to answer the first question, Aiken clay loam was shaken with 0.01 *M* $CaSO_4$ and 0.01 *M* $MgSO_4$. As in the case of zinc sulfate, 10-gm. samples were shaken with 100 ml. of solution. The results for calcium, magnesium, and zinc are shown in figure 2. It will be noted that the amounts of calcium and magnesium retained by the soil are much less than for zinc. This is partly due to the fact that the soil already contained 4.2 me. of exchangeable calcium and

1.4 me. of exchangeable magnesium. The point of interest, however, seems to be the shape of the curves for calcium and magnesium, which are somewhat different from the zinc curve. In other words, zinc apparently does not behave in the same way as the more common divalent cations.

To answer the second question above, three experiments were performed.

First, a quantity of Aiken soil was ground in a ball mill for 72 hours in the air-dry condition. Ten gram samples of this ground soil were then shaken with 0.01 *M* $ZnSO_4$ solution as usual. The results are presented in figure 3 together with the curve from figure 1 for Aiken. The sorption curve for the ground soil is parallel to that for the unground Aiken, but the amount of zinc sorbed increased as a result of grinding. This increase is to be expected, since it has been shown that grinding commonly increases the exchange capacity of kaolinitic materials. Grinding would tend to break down not only the aggregates but also the platelets of the clay minerals. If grinding is assumed to have increased the surface area as evidenced by the greater sorption of zinc, equilibrium has not been established during the early hours of shaking, which is the important point.

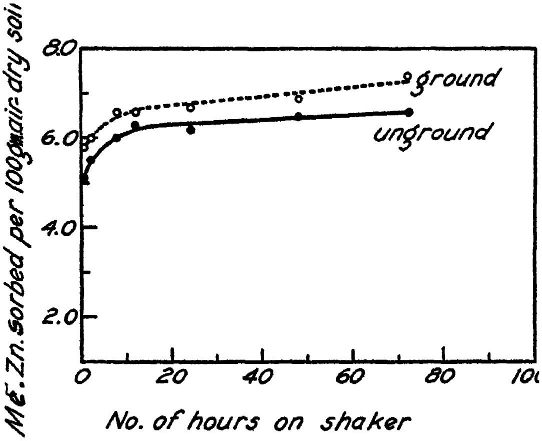

FIG. 3. SORPTION OF ZINC BY GROUND AND UNGROUND AIKEN CLAY LOAM

In a second experiment, 10-gm. samples of unground Aiken soil were moistened with distilled water and allowed to stand 48 hours in stoppered flasks before addition of the 0.01 *M* $ZnSO_4$ solution and shaking.

A third experiment consisted of two series run simultaneously. In the one series 10-gm. samples of unground Aiken soil were shaken with 99 ml. of distilled water plus 1 ml. of *M* $ZnSO_4$ solution. In the second series the 10-gm. samples of unground soil were shaken with 99 ml. of distilled water for 48 hours, after which 1 ml. of *M* $ZnSO_4$ solution was added to each and shaking continued. The shaking times and the results of the zinc determinations from experiments 2 and 3 are shown in figure 4.

From figure 4 it is apparent that premoistening and shaking in water for 48 hours prior to addition of $ZnSO_4$ did not significantly alter the trend of the sorption curve. It seems safe to assume, therefore, that the increase in zinc sorbed especially during the first hours of shaking is not due entirely to an increase in surface area of the clay particles. However, the more gentle slopes of all the curves in figure 1, that is, from 24 hours on, could very well be due to an increasing surface area, since it was observed in all soils that as shaking continued filtration became slower. It is also worthy of note that even after 6 days of shaking the soils continued to sorb zinc, although only in small amounts.

Organic matter is known to have exchange properties and, so that the effect of this fraction of the soil might be eliminated or materially diminished in studying zinc sorption, about 150 gm. of Aiken clay loam were treated with 135 ml. of 15 per cent H_2O_2. The whole was evaporated to a small volume, taken up in 95 per cent ethyl alcohol, filtered, and washed with alcohol. Finally, the soil was

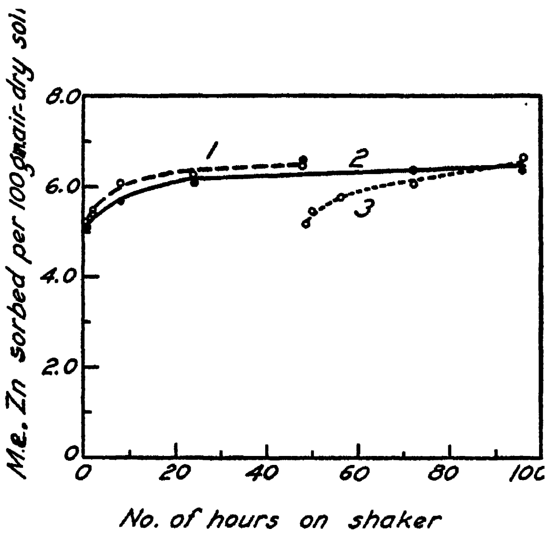

FIG. 4. SORPTION OF ZINC BY AIKEN CLAY LOAM AS AFFECTED BY PREMOISTENING AND AGITATING IN DISTILLED WATER

1, $ZnSO_4$ solution added to premoistened soil; 2, H_2O and $ZnSO_4$ solution added at start of shaking; 3, H_2O added, shaken for 48 hours, $ZnSO_4$ solution added and shaking continued.

dried and pulverized. Ten-gram samples of this H_2O_2-treated soil were shaken with 0.01 *M* $ZnSO_4$ solution as usual and the filtrates analyzed for zinc. The results are given in figure 5.

The sorption curve for the peroxide-treated Aiken does not have the same characteristics as the untreated soil shows in figure 1. The peroxide-treated soil sorbed 5.7 me. of zinc during the first 0.5 hour of shaking, as compared to 5.1 me. for the untreated soil. Also the curve in figure 5 indicates that after 8 hours' shaking, a maximum has apparently been reached. It should also be pointed out that the final amount of zinc sorbed by the peroxide-treated soil, that is, after 48 hours, is lower than in the untreated Aiken. These results are consistent with the findings of other investigators.

RELEASE OF ZINC FROM ZN-AIKEN CLAY LOAM

To investigate the ease of replacement of zinc, a Zn-Aiken soil was prepared by leaching with 0.2 *N* zinc acetate solution adjusted to a pH of 6.0 with acetic acid. Excess zinc acetate was leached out with 60 per cent ethyl alcohol, and finally the soil was dried and pulverized.

The release of zinc was first studied by equilibrium extracts. Thus, 10-gram. samples were shaken with 0.01 *M* H_2SO_4, 0.01 *M* K_2SO_4, and 0.01 *M* $MgSO_4$, filtered, and the filtrate analyzed for zinc as in the case of the sorption studies.

The results are shown in figure 6. The curve for the release of zinc with 0.01 *M* H_2SO_4 has a shape similar to that of the sorption curve (fig. 1). Perhaps more significant is the fact that the sulfuric acid released more zinc than is represented by the exchange capacity as determined with ammonium acetate. Magnesium and potassium are much less effective in replacing zinc than hydrogen, which is to be expected.

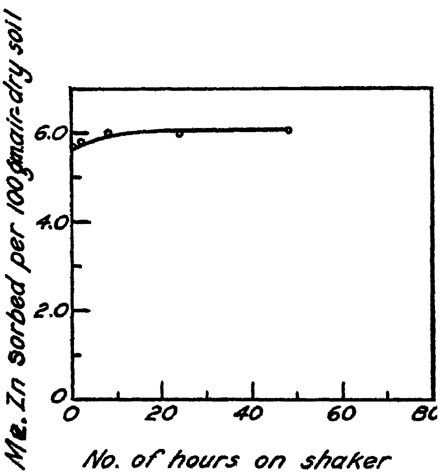

FIG. 5. SORPTION OF ZINC BY H_2O_2-TREATED AIKEN CLAY LOAM

To investigate the total amount of zinc replaceable, the Zn-Aiken was leached with several reagents. In these studies 10-gm. samples were usually leached with 500 or 1,000 ml. of the reagent. In some cases the exchange capacity was determined subsequently with neutral normal ammonium acetate. The leachate was then evaporated to dryness and treated with concentrated HNO_3 to destroy organic matter. After removal of the SiO_2, iron, and aluminum by appropriate methods, the zinc was titrated with ferrocyanide as previously. The reagents used and the milliquivalents of zinc released are presented in table 1. Exchange capacities, where determined, are also given.

Table 1 shows that ammonium acetate replaced 12.06 me. of zinc, which is only slightly above the exchange capacity as subsequently determined. It should be pointed out that the exchange capacity, as determined with ammonium acetate, for untreated Aiken was 12.1. According to Elgabaly and Jenny (4) and

Bower and Truog (1) the milliequivalents of zinc released by ammonium acetate might be expected to be higher than the exchange capacity. However, their studies were with montmorillonite, and the results reported herein are on Aiken soil, which is kaolinitic. Perhaps kaolinitic material does not adsorb zinc in the same way as montmorillonite. There may also be a small admixture of two or more clay minerals in the Aiken soil that have properties unlike montmorillonite.

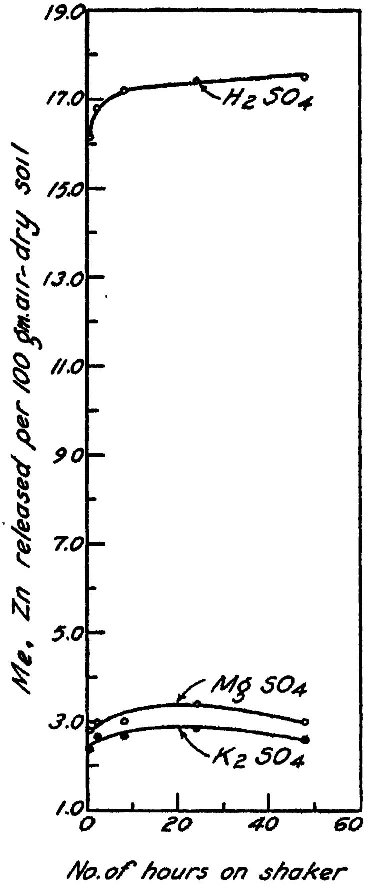

FIG. 6. RELEASE OF ZINC FROM ZN-AIKEN CLAY LOAM

Ammonium sulfate, magnesium acetate, and barium acetate replaced similar amounts of zinc, namely 10.41, 10.32, and 10.66 me. respectively. These values are all lower than the zinc replaced by ammonium acetate. It was observed that all four reagents gave similarly yellow colored leachates; the solubility of organic matter did not appear to be very different in these solutions.

With increasing acidity of the leaching solution, the amount of zinc released increased to more than twice the exchange capacity as determined with ammonium acetate. Elgabaly and Jenny (4) found that only 70 per cent of the adsorbed zinc could be released from montmorillonite with hydrochloric acid at 4S concentration. As acetic acid gave similar results to sulfuric acid, the anion apparently had little, if any, effect on the release of the zinc.

The main question that arises from the data presented in table 1 seems to be concerned with the relatively high value for zinc released by 0.02 *N* H_2SO_4 and 5 *N* acetic acid.

To ascertain the reproducibility of the results obtained for the release of zinc by H_2SO_4 four 10-gm. samples of untreated Aiken soil were leached with 500 ml. of 0.5 *N* zinc acetate solution adjusted as previously to pH 6.0. After the excess zinc acetate was leached out with 60 per cent ethyl alcohol, the zinc was replaced by leaching with 1 liter of 0.02 *N* H_2SO_4. Zinc was subsequently determined on the acid leachates, which revealed that this strength of sulfuric acid had released 28.63, 28.04, 27.40, and 27.52 me. of zinc per 100 gm. of air-dry soil. These values are all higher than the 24.09 me. reported in table 1, but they are of the same order of magnitude.

TABLE 1

Release of zinc from Zn-Aiken by various reagents and the subsequent exchange capacities with ammonium acetate

REAGENT	Zn RELEASED PER 100 GM. AIR-DRY SOIL	EXCHANGE* CAPACITY WITH AMMONIUM ACETATE
	me.	*me.*
500 ml. *N* neutral ammonium acetate	12.06	11.7
500 ml. *N* neutral magnesium acetate	10.32	12.2
500 ml. *N* neutral ammonium sulfate	10.41	—
500 ml. *N* neutral barium acetate	10.66	10.1†
6 liters 0.0005 *N* H_2SO_4	15.93	12.8
1 liter 0.02 *N* H_2SO_4	24.09	12.4
1 liter 5 *N* acetic acid	24.86	—

* Exchange capacities determined by J. M. Rible, Senior Laboratory Technician, University of California.

† As determined by replacing the Ba with HCl and precipitating as $BaSO_4$.

There are at least three possible explanations for the high values obtained with the 0.02 *N* H_2SO_4 and 5 *N* acetic acid:

First, it has been suggested (4) that zinc may be adsorbed as a divalent Zn^{++} ion or as univalent ions such as $(ZnOH)^+$ or $(ZnCl)^+$. If this is the case, then there is a possibility that neutral normal salt solutions released only divalent zinc, whereas the sulfuric and acetic acids could also release the univalent ions.

A second hypothesis concerns an organic matter relationship. It was observed that the leachates from 0.02 *N* H_2SO_4 as well as those from 5 *N* acetic acid were more highly colored than those from any of the other reagents. This has not been explored to the fullest extent, but in view of the fact that only a small quantity of organic matter may produce a highly colored extract, it seems improbable that a value of 12 me. could be attributed to this organic fraction. Since organic matter in soils supposedly possesses exchange properties, then, certainly zinc adsorbed by this fraction should be at least in part exchangeable with neutral salt solutions. Jones, Gall, and Barnette (6) found that addition of 1 per cent peat to Norfolk sand increased both the amount of zinc fixed by the soil and the replaceable zinc. Further doubt on the organic matter mechanism comes from the fact that 0.02 *N* H_2SO_4 released some 21.4 me. from a Zn-Aiken after being treated with H_2O_2.

A third hypothesis is that perhaps a portion of the zinc was precipitated as $Zn(OH)_2$ or other inorganic zinc compound or as a zinc organic compound which was not subsequently leached out with 60 per cent alcohol or extracted with neutral normal salt solutions.

There are, however, valid reasons for doubting the completeness of this third explanation. Zinc precipitated as $Zn(OH)_2$ or $ZnCO_3$ should be somewhat soluble in ammonium salt solutions, especially where a leaching technique is employed. Exchange data in table 1 do not suggest any increase over the exchange capacity when Zn-Aiken was leached with either $(NH_4)_2SO_4$ or ammonium acetate. If the basic carbonate $2ZnCO_3 \cdot 3Zn(OH)_2$ formed, however, it may not be so readily soluble in the neutral salt solutions but could dissolve in the 0.02 *N* H_2SO_4. The alcohol washing, in preparing the Zn-Aiken, was considered complete when the filtrate gave no test for zinc. Thus, if a sparingly soluble compound of zinc were present in the soil, continued washing should leach virtually out all of it.

Then too, Elgabaly and Jenny (4), as already pointed out, found that HCl was not so effective in releasing zinc as was ammonium acetate. They had used a procedure similar to the one outlined in the present paper in preparing a zinc montmorillonite.

It seems reasonable to suggest that perhaps all three of the explanations presented are important in the mechanism of zinc sorption. Isomorphous replacement by zinc may also account for some of the results obtained, although one would not expect much replacement of this type to occur in kaolinitic materials.

Some interesting studies suggest themselves concerning the availability of zinc in this Zn-Aiken soil. It seems entirely possible that plants could utilize more zinc than is represented by the exchange capacity. According to table 1, 0.0005 *N* H_2SO_4, which represents a pH of 3.5, released more zinc than did the salt solutions, and the pH of the soil solution in the immediate vicinity of plant roots is thought to be near to or slightly below this value.

SUMMARY

The sorption and release of zinc by Aiken clay loam have been studied. Data on the sorption of zinc by several other soils are included for comparison. It has been shown that the sorption of zinc by Aiken is somewhat different from that of other soils and that the sorption of calcium and magnesium is unlike that of zinc. Grinding, premoistening, and agitating in water prior to addition of $ZnSO_4$ solution failed to alter the shape of the sorption curve. The type of curve obtained suggests that other factors are involved in the sorption of zinc besides an exchange mechanism.

The release of zinc from a prepared Zn-Aiken also suggests more than an exchange phenomenon. Results presented also reveal that acid solutions are much

more effective in releasing zinc than are neutral normal salt solutions. Several hypotheses are put forth as possible explanations for the findings.

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EFFECT OF LONG-TIME CROPPING ON SOIL PROPERTIES IN NORTHEASTERN NEW MEXICO[1]

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The success of conservation measures and maintenance of soil productivity argely depend upon a thorough understanding of the effect of cropping on soil roperties. This problem has been investigated at the Rothamsted Experimental Station, England, and in many locations in the United States (1, 4, 7–10), but ittle information of this sort has been reported from New Mexico (2, 3). Al-hough no long-term experiments have been especially designed for estimating the inherent soil fertility in this state, there are cultivated fields, virgin sod, and bandoned farms on identical or closely related soil series in the Tucumcari region in northeastern New Mexico. This report presents the findings from a study of the effect of cultivation and cropping on the physical and chemical roperties and the nutrient-supplying level of these soils.

The author acknowledges with gratitude the cooperation and assistance endered to him during the progress of this study by Milton Fireman and L. W. Healton, U. S. Regional Salinity Laboratory, Riverside, California; D. R. Burnham, U. S. Dry Land Field Station, Tucumcari, New Mexico; Harrison J. Maker, Soil Conservation Service, State College, New Mexico; C. A. Grimes, ounty extension agent, and Wayne Miles, Soil Conservation Service, Tucum-ari, New Mexico.

DESCRIPTION OF THE AREA

In many respects, the major soil series of Tucumcari may be regarded as the western extension of the soil of the Panhandle of Texas, but the average annual recipitation at Tucumcari, 16.51 inches (3), is appreciably lower than the 21.01 nches at Amarillo, Texas, which represents the Panhandle. In terms of broad oil grouping, the soils may be classified as reddish chestnut, reddish brown, nd brown, with lime and gypsum accumulations at various depths. Parent aterials range from unconsolidated alluvial and aeolian sediments of the Quaternary or late Tertiary period to reddish brown sandstones and shales of the Triassic period. The native vegetation consists of mixed tall and short grasses and ccasional mesquite shrubs, yucca, and cacti. Plant ecologists generally regard his type of vegetative cover as "mixed prairie."

Cattlemen came in to the region from 1885 to 1895, and settlement of home-teads began about 1900. Even then, cattle grazing was the major occupation. There are, however, continuous experiment records back to 1923 on spotted dry-armed areas surrounded by sod, and the history of these areas can be traced with reasonably certainty to 1905. Irrigation of newly opened land in the western section of Tucumcari began in 1946 after completion of the Conchas Reservoir, which is situated on the upper Canadian River, approximately 30 miles northwest of Tucumcari. According to reliable information, fertilizers have never been used on the areas where soil samples were collected.

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[1] Contribution No. 57 from the New Mexico Agricultural Experiment Station.

MATERIALS AND METHODS

Soil samples were taken only from areas where cropped and virgin soils were of the same soil type and where authentic information about the history of the fields was available. Of the nine fields selected, four represented virgin soil, three had been continuously cropped for 19 to 36 years, and two had been abandoned to grass and weeds for 5 to 20 years.

An average of four soil samples per location were collected, by horizons, to a depth of 64 inches. These were air-dried, sieved, and analyzed for particle-size distribution, percentage aggregates below 0.05 mm., apparent density, field capacity, air porosity, total soluble salts, gypsum, lime, exchangeable bases, pH, total nitrogen, total organic matter, and available PO_4. Crop yields and nutrient-supplying ability of the soils were determined by pot culture under controlled greenhouse conditions. Only data of the first two horizons are included in this report.[2]

The particle-size distribution was determined by the improved Bouyoucos method; however, only the percentage of clay particles of effective diameter less than 2μ is given. The percentage of aggregates smaller than 0.05 mm. was calculated by the formula, $\frac{A-B}{A} \times 100$ in which A stands for the total silt plus clay determined by mechanical analysis, and B represents the same fraction determined without dispersion. The total porosity was calculated from apparent density determinations of soil cores taken at approximate field capacity.[3] The volume of liquid phase was calculated from sticky point determinations. The volume of gaseous phase is taken as the difference between the total porosity and liquid phase.

The soluble salts were calculated from chemical analyses of the saturation extract, and pH was determined on a saturated paste by means of the glass electrode. The base-exchange capacity was calculated from the quantity of ammonia distilled from the soil, which had been previously extracted with neutral ammonium acetate and then washed with alcohol. The exchangeable sodium was determined by the zinc uranyl acetate procedure from the acetate leachate. The percentage total nitrogen was determined by the Kjeldahl method. Phosphate was determined by the K_2CO_3 method of Hockensmith, Gardner, and Goodwin (6) and expressed in parts per million. Graham's (5) method was used to determine percentage organic matter. The C:N ratio was calculated by dividing 58 per cent of the organic matter by total nitrogen. Gypsum was determined by precipitation of $BaSO_4$ in a HCl extract. Lime was determined by CO_2 released with standard 0.5 *N* H_2SO_4 and back titrating with standard 0.5 *N* NaOH. The total nitrogen of the plant tissue was determined by the official A.O.A.C. method. The potash and phosphoric acid were determined by the sodium cobaltinitrite method and the standard molybdate method, respectively.

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[2] Except for the Dalhart series, the data on base-exchange capacity, exchangeable sodium, soluble salts, pH, total nitrogen, and available phosphate were obtained by Milton Fireman and L. H. Healton, who have kindly permitted the author to include their data.

[3] At least five determinations were made on each horizon from each soil except for the subsoils of cropped Tucumcari loam and virgin Dalhart fine sandy loam.

Since it is probable that no chemical method can substitute for the mechanism which plants have for extracting available nutrients from the soil, greenhouse pot experiments were used. Yields were calculated and the plant tissue was analyzed and interpreted in assessing soil fertility of cropped and virgin fields. The nutrient supplying ability was taken as the quantity of N, P_2O_5, and K_2O extracted from treated soil by an indicator plant (German millet) grown to the blooming stage under controlled greenhouse conditions. The N-supplying ability was taken as the total amount of nitrogen removed by the plants from soil which had been treated with P_2O_5 and K_2O at the equivalent rate of 100 pounds each per acre. The P_2O_5-supplying ability was estimated from the total quantity of P_2O_5 removed from soil which had been fertilized with N and K_2O equivalent to 100 pounds each per acre. Similarly, the total amount of K_2O which millet was able to remove from the soil that had received N and P_2O_5 applications is regarded as the K_2O-supplying ability of the soil.

CHANGES IN PHYSICAL PROPERTIES OF CROPPED SOILS

Table 1 indicates that the cropped soils and virgin soils within each soil series are very similar in clay content. Extensive mechanical analyses of all horizons have shown this to be the case throughout the entire profile. Soils of the Tucumcari, La Brier, and Quay series have medium-textured profiles, and soils of the Dalhart and Springer series have relatively coarse-textured profiles. On the average, the cropped and the virgin soils were not significantly different in the amount of clay smaller than 2 μ, although an incipient downward migration of clay particles in cropped soils seems to have taken place.

Cropping caused considerable change in soil aggregation. After an average of 22.4 years of cropping, the surface soil and the subsoil show average losses of 48 and 44 per cent, respectively, of their original aggregation (table 1). Loss of aggregation through cropping is greatly magnified in the finer-textured soils. The cropped Tucumcari loam has lost 81 per cent (topsoil) and 77 per cent (subsoil) of the aggregation found in the virgin Tucumcari loam. The high aggregation figure from the Springer soil which was abandoned for 20 years, as compared to the corresponding cultivated soil, suggests that native grass and weeds are very effective in restoring aggregation.

The average total porosity of both surface soils and subsoils has decreased somewhat under cropping. The useful, or available, moisture range in these soils could not be calculated because their permanent wilting points were not determined. The average moisture content of the surface horizon at the field capacity is 15 per cent lower in cropped than in virgin soils, and it is 17 per cent lower in

TABLE 1

Physical and chemical properties of virgin and cropped soils

SOIL TYPE	LAND USE*	DEPTH	CLAY $<2\mu$	AGGREGATES LESS THAN 0.05 MM.	LIQUID PHASE	GASEOUS PHASE	TOTAL POROSITY	BASE-EXCHANGE CAPACITY‡	EXCHANGEABLE SODIUM‡	SOLUBLE SALTS‡	pH‡	LIME	GYPSUM
		in.	%	%	%†	%†	%†	*me./100 gm.*	%	%		%	%
Dalhart fine sandy loam	Virgin sod	0–4	8.2	58.4	24.4	16.9	41.3	8.8	1.6	.03	7.9	0.3	0
		4–14	11.4	63.4	24.1	15.8	39.9	10.9	1.4	.04	7.8	0.4	0
	Cropped 19 years	0–6	11.6	41.9	19.9	16.5	36.4	6.4	2.0	.02	7.6	0.2	0
		6–20	16.8	56.5	24.8	13.1	37.9	11.3	1.7	.02	7.5	0.4	0
Mixed Quay and La Brier loam	Virgin sod	0–8	20.3	88.5	27.6	16.8	44.4	14.7	1.0	.01	7.6	1.4	0
		8–18	23.6	90.4	32.2	11.1	43.3	18.9	0.8	.01	7.6	3.0	0.1
	Cropped 36 years	0–4	19.4	41.9	25.5	15.5	41.0	13.2	2.0	.01	7.8	1.1	0
		4–11	21.0	42.7	23.8	20.2	44.0	11.8	0.5	.02	7.7	1.6	0.1
Springer fine sandy loam	Virgin sod	0–12	12.0	52.0	23.6	12.4	36.0	9.2	2.2	.01	7.8	0.3	0
		12–24	11.8	44.2	26.0	16.9	42.9	11.5	1.3	.01	7.6	0.5	0.1
	Cropped 5 years§	0–9	9.4	51.3	19.6	12.4	32.0	9.9	1.4	.01	7.8	0.6	0
		9–20	11.8	45.2	20.2	12.1	32.3	11.2	1.4	.01	8.1	1.3	0.1
	Cropped 32 years	0–10	9.6	34.0	21.0	15.2	36.2	9.3	0.9	.01	8.0	1.5	0
		14–27	13.6	38.5	20.3	15.8	36.1	11.5	—	.03	8.4	2.6	0.3
Tucumcari loam	Virgin sod	0–7	19.9	89.1	27.3	18.7	46.0	14.5	1.2	.01	7.9	0.7	0
		7–12	24.4	92.5	33.8	18.7	52.5	13.4	1.0	.01	7.7	1.8	0.2
	Cropped 20 years¶	0–9	18.0	17.0	23.6	23.6	47.2	15.7	2.4	.01	7.7	0.3	0
		9–18	25.4	21.0	31.9	9.5	41.4	19.8	2.5	.02	8.0	1.4	0.1

Average of all soils	Virgin sod	Topsoil	15.1	72.0	25.7	16.2	41.9	11.8	1.5	.015	7.8	0.68	0
		Subsoil	17.8	72.6	29.0	15.6	44.7	13.7	1.1	.018	7.7	1.43	0.1
	Cropped 22.4 years	Topsoil	13.6	37.2	21.9	16.6	38.6	10.9	1.7	.012	7.8	0.74	0
		Subsoil	17.7	40.8	24.2	14.1	38.3	13.1	1.5	.020	7.9	1.46	0.1

* Irrigation was begun in 1947 on every cropped field except the one in the Dalhart series, which is still dry-farmed.

† By volume.

‡ Data, except for those on Dalhart soils, were obtained from Milton Fireman and L. W. Healton, "Investigation of salinity and alkali conditions of soil of the Tucumcari project, New Mexico." Mimeographed, U. S. Regional Salinity and Rubidoux Laboratories, 1948.

§ This field has been abandoned to grasses for 20 years.

¶ This field was abandoned to grasses for 5 years before it was broken out for irrigation in 1947.

the cropped subsoils. The average volume of gaseous phase of virgin soils at field capacity is very like that of the cropped soils.

CHANGES IN CHEMICAL PROPERTIES OF CROPPED SOILS

The chemical data are summarized in table 1 and in table 2. From the data, it seems that long-time cropping has had almost no effect on the pH, lime, and gypsum status of these soils. Moreover, long-time cropping has had no significant effect on the base-exchange capacity. The 7.6 per cent decline in exchange capacity which did occur in cropped (surface) soils appears to be caused by the loss of organic matter. The percentages of exchangeable sodium, on equivalent basis, are generally higher in cropped soils than in the corresponding virgin soils. The total soluble salts, on the other hand, are slightly lower in the cropped surface soils. Since both the absolute and the relative differences are very small, these differences cannot be attributed to the selective absorption of plants.

The over-all lack of significant changes in chemical properties is not difficult to explain. The quantity of minerals removed by dry-farmed crops is nominal as compared with the potential supply of the base-saturated soils. This fact and its interpretation are supported by the work of Botkin and Smith (2). Furthermore, under the conditions of limited rainfall, leaching has not caused apparent chemical changes in cropped soils.

CHANGES IN NUTRIENT STATUS OF CROPPED SOILS

Pot culture results and additional chemical data which may be more closely related to soil fertility are summarized in table 2. These figures indicate that cropping has brought about a decrease of 44 per cent in organic matter, 31 per cent in total nitrogen, 26 per cent in available phosphates, and 18 per cent in C:N ratio in the soils of the surface horizon. They further show that in the subsoils cropping has brought a decrease amounting to 31 per cent for the organic matter, 28 per cent for nitrogen, 23 per cent for phosphates, and 6 per cent for the C:N ratio. Over a period averaging 22.4 years the annual rate of loss in the surface soil of organic matter and total nitrogen appears to be 2.0 per cent and 1.4 per cent of the original amounts present, respectively.

The quantity of N, P_2O_5, and K_2O removed by plants under the specified conditions, expressed as pounds per acre, are given in table 2. In the surface samples, the uptake of nutrients by plants was higher from the virgin soils than from the cropped soils. The uptake of nitrogen from the virgin sod was twice as high as that from the cropped soil; the uptake of P_2O_5 was 1.7 times as high as from the cropped; and the uptake of potash was only 1.2 times as high as from the cropped. The total uptake of K_2O is high compared with the uptake of nitrogen and phosphoric acid.

The nutrient uptake by plants from subsoils was obtained from only one soil series, and therefore may not represent the entire area. The limited data suggest, however, that continued dry-farming has depleted the fertility of surface soils only.

In spite of the amount of available phosphates removed from the surface

TABLE 2

Nutrient status of virgin and cropped soils

SOIL TYPE	LAND USE*	DEPTH	TOTAL NITROGEN†	AVAILABLE PHOSPHATE†	ORGANIC MATTER	C:N RATIO	NUTRIENT UPTAKE‡		
							N	P_2O_5	K_2O
		in.	%	*ppm.*	%		*lb./A.*	*lb./A.*	*lb./A*
Dalhart fine sandy loam	Virgin sod	0–4	.074	66	1.38	10.8	40.7	30.4	189.0
		4–14	—	35	—	—	31.0	5.9	183.1
	Cropped 19 years	0–6	.052	29	0.77	8.7	23.3	24.4	149.5
		6–20	—	18	—	—	28.9	5.3	179.2
Mixed Quay and La Brier loam	Virgin sod	0–8	.076	62	1.49	11.5	57.9	16.0	184.7
		8–18	.061	40	0.96	9.0	—	—	—
	Cropped 36 years	0–4	.045	32	0.66	8.4	21.6	4.5	138.7
		4–11	.038	22	0.46	7.0	—	—	—
Springer fine sandy loam	Virgin sod	0–12	.052	40	0.96	10.7	22.9	10.4	168.8
		12–24	.035	24	0.53	8.7	—	—	—
	Cropped 5 years§	0–9	.044	30	0.76	10.0	20.1	8.3	157.7
		9–20	.050	28	0.73	8.6	—	—	—
	Cropped 32 years	0–10	.049	46	0.65	8.0	15.3	4.4	127.9
		14–27	.028	11	0.36	7.6	—	—	—
Tucumcari loam	Virgin sod	0–7	.105	46	1.82	10.1	56.8	7.0	161.2
		7–12	.100	28	1.32	7.7	—	—	—
	Cropped 20 years¶	0–9	.071	60	1.14	9.3	29.8	5.2	150.8
		9–18	.071	44	1.05	8.6	—	—	—
Average of all soils	Virgin sod	Topsoil	.077	53.5	1.43	10.8	44.6	16.0	176.0
		Subsoil	.065	31.8	0.94	8.5	31.0	5.9	183.1
	Cropped 22.4 years	Topsoil	.053	39.4	0.80	8.9	22.0	9.4	144.9
		Subsoil	.047	24.6	0.65	8.0	28.9	5.3	179.2

* Irrigation was begun in 1947 on every cropped field except the one in the Dalhart series, which is still dry-farmed.

† Data, except for those on Dalhart soils, were obtained from Milton Fireman and L. W. Healton, "Investigation of salinity and alkali conditions of soil of the Tucumcari project, New Mexico." Mimeographed, U. S. Regional Salinity and Rubidoux Laboratories, 1948.

‡ Quantities of N, P_2O_5, and K_2O extracted by growing German millet to blooming stage under controlled greenhouse conditions.

§ This field has been abandoned to grasses for 20 years.

¶ This field was abandoned to grasses for 5 years before it was broken out for irrigation in 1947.

horizon by cropping, it appears that more available phosphates still remain in the surface than in the subsoil horizons of these soils. The loss of nitrogen is generally associated with the loss of organic matter. The figures indicated, however, that the uptake of P_2O_5 is more closely related to the soil organic matter than to the amount of chemically available phosphate in the soil. This is illustrated by the data from Springer fine sandy loam. The P_2O_5 uptake from a cropped field abandoned to grass and weeds for 20 years was 8.3 pounds per acre—3.9 pounds more than the per-acre uptake from the continually cropped Springer fine sandy loam. On the other hand, there was more chemically available phosphate in the continually cropped field than in the abandoned field.

DISCUSSION

The most pronounced change in physical properties of soil under cropping is the loss of original aggregation in the upper horizons. This loss of aggregation averaged 48 per cent, ranging from 81 per cent in the heavier Tucumcari loam to 28 per cent in the lighter Dalhart fine sandy loam. This average compares with a 27 per cent loss in the "state of aggregation" of Marshall silty clay loam in eastern Nebraska as a result of 50 years' cropping (1) and an 80 per cent loss of aggregation in a heavy Colby, or Crete, clay at Hays, Kansas, as a result of 40 years' cropping (9). On the other hand, the decreases in water-retaining capacity, total porosity, and air capacity (gaseous phase) of the Tucumcari soils were not so large as those reported in western Oregon (15), eastern Nebraska (1), and western Ohio (10). Apparently, the climate, soil conditions, and methods of farming may influence the trend and magnitude of changes in soil properties.

On a percentage basis, the decline in organic matter and total nitrogen under cropping appears to be more rapid in this region than in the Midwest (7), the Great Plains (14), or western Oregon (15). The high temperature in Tucumcari soil may be responsible for the rapid loss.

The fact that the organic matter is being depleted more rapidly than the total nitrogen in the surface soil points to a gradual narrowing of the C:N ratio. As the ratio narrows, the limited energy factor will retard the process of decomposition and stabilize the humus at a new equilibrium level. Graphs prepared by the author relating the rate of loss of organic matter to the number of years of cropping suggest that the rate has declined to a minimum in about 20 years, and that a new equilibrium may have been established within 30 years under Tucumcari conditions.

A critical C:N ratio is reached when the rates of decomposition of organic matter and release of nitrogen appear to slow down materially. If the ratio is substantially lowered below the critical point by continuous cropping without the use of fertilizers, the physical properties and nutrient status of the soil may be jeopardized because of poor aggregation and slow release of nutrients. As a matter of fact, two fields, one in the Springer series and the other in the Tucumcari series, were once abandoned after 5 to 20 years of farming, presumably because of the loss of organic matter and fertility. This might have been corrected by use of fertilizers. Previous work[4] indicates that the critical C:N ratio for most Tucumcari soils is about 9.0. The average C:N ratios for virgin and cropped

[4] Details being published by the New Mexico Agricultural Experiment Station.

soils are 10.8 and 8.9 respectively. From the standpoint of soil fertility, it is important to maintain the C:N ratio above the critical level. It should be pointed out that the climatic conditions of the irrigated fields are different from those of the adjacent dry-farmed fields, largely because of the difference in moisture. The C:N ratio of irrigated soils, according to Powers (12) and Jenny (8), should be higher than the adjacent dry-farmed soils.

The influence of native grasses and weeds upon the restoration of soil fertility and aggregation is reflected in the data obtained from the abandoned field of the Springer series. Thus the aggregation of the abandoned field was 99 per cent of that of virgin sod, as contrasted with 65 per cent in the cropped area; N-supplying ability was 88 per cent as contrasted with 67 per cent; and P_2O_5-supplying ability was 80 per cent and 42 per cent. Rotation with sod is believed to be the main factor in maintenance of soil fertility on old continents like Europe and Asia. In California (11), 8 years of mustard and volunteer weeds restored the infiltration rate and productivity of an experimental orchard to the original condition. At Hays, Kansas (9), 5 years of irrigated and 25 years of dry-farmed buffalo grass restored the aggregation of depleted soils from 20 per cent to 60 per cent and 100 per cent respectively of the corresponding virgin soils. This effect is by no means limited to the West. For example, 29 years of native grasses on the Morrow plots in Illinois (4) and 30 years of grass and weeds supplemented with potash and phosphate on a New Jersey experimental plot (13) also resulted in restoration of deteriorated soils to their original nutrient levels.

SUMMARY

Extensive physical measurements, chemical analyses, and biological tests were conducted on approximately 100 samples of soil collected from horizons of cropped and virgin fields of Tucumcari loam, mixed Quay and La Brier loam, Dalhart fine sandy loam, and Springer fine sandy loam.

After an average of 22 years under cropping, these soils show a considerable decline in their physical suitability for agricultural purposes (indicated by aggregation, porosity, and water-retaining capacity) and in organic matter, total N, and nutrient-supplying ability. Chemical differences between cropped and virgin soils are often inadequate to account for differences in productivity.

The relative loss of organic matter and total nitrogen indicated humus stabilization at a new equilibrium in cropped soils. The critical C:N ratio for Tucumcari soils was approximately 9.0; the C:N ratio averaged 8.9 for the cropped soils and 10.8 for the virgin soils.

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EFFECTS OF CARBON BLACK ON THE PROPERTIES OF SOILS: II. EFFECTS ON HUMID SOILS[1]

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Although the carbon blacks used in this work have little nutrient value for plants, they cause changes in the soil which may induce better plant growth. Carbon blacks are in the colloidal state of division and carry a charge. When mixed into light colored soils, in proportions of 1 part in 250 or more parts, they darken the soils considerably. Stimulation of plant growth in humid soils is thought to be associated with added energy due to darkening and to more favorable aggregation caused by the charge on the colloidal particles. Other finely divided black substances would no doubt exhibit similar effects. For research purposes, however, carbon blacks have the advantage that the results produced by darkening and fine size may be evaluated without the confusion which results in attempting to dissociate growth produced by nutrient-containing blacks such as charcoal, scotch, soot, or lignite.

Three types of carbon black were used in these experiments. Their important properties are described in table 1.

Merrimac fine sandy loam containing 3.5 per cent clay was used in most of the tests. Cheshire fine sandy loam containing 9 per cent clay was used in other tests. The frost removal tesss were made on Agawam fine sandy loam. Fertilizer, usually 7-7-7, has been added to all soils at the rate of 200 pounds of nitrogen per acre. "Untreated soil" refers to soil containing this fertilizer but not treated with carbon.

MOISTURE CONTENT OF SOILS IN THE FIELD

Since soil temperature is affected by moisture relations in the soil, temperature data described in the previous paper[3] were supplemented by moisture measurements made according to standard procedures[4]. Measurements were made regularly during a drought from August 3–17, 1944, and also whenever unusual conditions occurred.

Table 2 lists average moisture content of field samples of the carbon-treated and the untreated Merrimac soil. Carbon application was 4,000 pounds Elf 3 per acre.

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[2] Assistant professor, agronomy department, University of Massachusetts, and assistant to director, research and development department, Godfrey L. Cabot, Inc., respectively.

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Morning moisture readings were almost uniformly 10 per cent higher in carbon-treated soils than in untreated soil throughout the August hot dry spell. The single afternoon reading made during the hot spell showed 4 per cent higher moisture in the carbon-treated soil. Other morning moisture readings taken were all higher on carbon-treated soil than on untreated soil; the minimum difference was 1.3 per cent. Early afternoon readings showed higher moisture in carbon-treated soil in five out of six cases.

TABLE 1

Properties of carbon blacks

	STERLING R STERLING S	ELF 3	MOGUL
Grade*	Semi-reinforcing Furnace (SRF)	Low color channel (LCC)	Long-flow impingement (LFI)
Description	Gas furnace	Channel	After-treated channel
pH	9- 10	4-5	2-3
Surface area by nitrogen adsorption, *sq. m./gm.*	30- 40	100-170	150-200
Average particle size, A	700-900	170-250	200-250
Carbon, *per cent*	98-99	95	92
Hydrogen, *per cent*	0.2-0.4	0.5-0.7	0.4
Oxygen, *per cent*	0.3-0.9	2-4	7-8

SPECTROSCOPIC ANALYSIS STERLING (All less than 0.1 per cent)	ELF 3 AND MOGUL IMPURITIES
B Ca Cr Fe K Mg Mn Na Si Sn Sr Ti	H_2, CO, CO_2, H_2O and traces of hydrocarbons are present

* Trade names are those of Godfrey L. Cabot, Inc., who supplied the carbon blacks tested. Grade designations are those used in the carbon black industry.

WET AND DRY AGGREGATION OF SOILS

Fifty-gram samples of untreated soil and of soil treated with a definite percentage of carbon black were dispersed, each in 1 liter of water, for 5 minutes with a blade mixer at 3,500 r.p.m. After they had settled for 1 hour, a 25-cc. sample of the liquid in each was removed with a pipette tip at the appropriate level, as calculated by Stoke's law. Evaporation and ignition of this sample left a residue representing the unflocculated clay (<0.002 mm.) in the soils. Untreated Merrimac soil containing 3.5 per cent clay was found to contain 1.5 per cent unaggregated clay. Merrimac soil treated with 0.2 per cent Elf 3 carbon, pH 4, showed no unaggregated clay.

As the liquid dispersion in this test contained an excess of carbon, lower concentrations of carbon were investigated with the same soil. Concentrations down to and including 0.06 per cent Elf 3 (600 ppm. C) completely flocculated all clays in the soil. This agrees with work by Perotti and Ruso[5] in which 1,200 pounds of charcoal per acre caused aggregation.

TABLE 2

Field moisture content of carbon-treated and untreated soil samples

Carbon treatment at 4,000 pounds Elf 3/acre

DATE (1944)	TIME	MOISTURE CONTENT			WEATHER
		C-treated soil	Untreated soil	Increase in C-treated soil	
		per cent	*per cent*	*per cent*	
May 10	8 a.m.	20.1	18.8	1.3	
May 10	1 p.m.	12.6	17.8	−5.2	
June 20	8 a.m.	32.6	22.7	9.9	After rain
June 29	1 p.m.	39.4	21.5	17.9	
July 11	1 p.m.	26.5	20.3	6.2	
July 19	1 p.m.	16.1	10.8	5.3	
July 23	8 a.m.	45.0	35.0	10.0	
Aug. 3	8 a.m.	34.6	20.6	14.0	After rain, hot
Aug. 3	1 p.m.	30.2	20.6	9.6	
Aug. 4	8 a.m.	43.0	34.0	9.0	No rain, hot
Aug. 5	8 a.m.	41.0	32.0	9.0	No rain, hot
Aug. 6	8 a.m.	45.0	35.0	10.0	No rain, hot
Aug. 7	8 a.m.	45.0	35.0	10.0	No rain, hot
Aug. 8	8 a.m.	44.0	33.0	11.0	No rain, hot
Aug. 9	8 a.m.	43.0	31.0	12.0	No rain, hot
Aug. 10	8 a.m.	41.0	30.0	11.0	No rain, hot
Aug. 12	8 a.m.	40.0	29.0	11.0	No rain, hot
Aug. 13	8 a.m.	38.0	28.0	10.0	No rain, hot
Aug. 13	1 p.m.	18.4	14.4	4.0	No rain, hot
Aug. 14	8 a.m.	37.0	27.0	10.0	Rain
Aug. 15	8 a.m.	36.0	26.0	10.0	No rain, hot
Aug. 16	8 a.m.	36.0	25.0	11.0	No rain, hot
Aug. 17	8 a.m.	35.0	25.0	10.0	Rain

Untreated Cheshire soil containing 9.0 per cent clay showed 2 per cent unaggregated clay by this test. A sample of Cheshire soil treated with 0.2 per cent

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[5] PEROTTI, R., and RUSO, C. Studi concornenti l'azione del carbona sulla vegetazione: II. *Bol. Ist. Agr. Pisa* 4: 463–501. 1928.

Sterling S was completely flocculated to larger than clay size. An excess of carbon black was again present.

Separate tests were carried out on dry aggregation of these soils. Air-dried samples of the soils were shaken for 5 minutes in a Ro-Tap sieve shaker. The particles smaller than 1 mm. were as follows: Untreated Merrimac soil, 9.5 per cent; Merrimac soil treated with 0.2 per cent Elf 3 carbon, pH 4, 6.2 per cent; untreated Cheshire soil, 8.2 per cent; Cheshire soil treated with 0.2 per cent Sterling S carbon, pH 9, 5.8 per cent.

These studies, which were made in 1944 and 1945, showed that carbon had an aggregating effect on some soils, by both wet and dry tests, whether the carbon used was acid or alkaline.

Similar tests, using Sterling S black with boulder clay and Suffield soil, gave negative results in 1947 and 1948. In absence of further data, the conclusion is that some carbon blacks will cause aggregation in some soils.

ACCUMULATION OF SALTS NEAR SOIL SURFACES

To measure the comparative accumulation of salts near the surface of carbon-treated and untreated soil, a Solu-bridge, which is a modified Wheatstone bridge, was used to measure the conductivity of the salts leached from field samples. Carbon treatment on these samples was with Sterling S, 2,000 pounds per acre mixed to 2 inches. Samples of soil (50 gm. each) were taken from the upper ½-inch of the carbon-treated and untreated soil and shaken with 100 ml. of distilled water. The soil was filtered off after 15 minutes extraction, and the conductivity of the resulting solution measured. Conductivity is in direct proportion to the ionic concentrations of the salts extracted from the soils. Conductivities were recorded of four such measurements made between July 13 and August 17, 1947. The results were 12 per cent, 150 per cent, 46 per cent, and 85 per cent higher in the extracts from carbon-treated soils than in those from untreated soil. Other tests showed the same trend.

During the hot dry days of August 1944, an important special effect was observed in connection with salt accumulation. During this period, the carbon-treated soil (Elf 3, 4,000 pounds per acre, surface applications and 2-inch mix) was damper than untreated soil, as usual, in the morning, and both dried out considerably during the day (see table 2). During the day, however, most of the carbon-treated soil showed a whitened surface. Nitrate tests at the surface indicated that this whitening was due to accumulation of calcium and sodium nitrates at the surface. Carbon-treated soil showed accumulation of 1,000 ppm. NO_3-N as against 150 ppm. on untreated soil.

A secondary effect of this surface salt accumulation was that the heat intake was lowered. This lowered the maximum temperature of the carbon-treated soil surface enough to make the average daily maximum for August lower than the average maximum of the untreated soil surface. This was the only month in the summer periods under consideration for which this was the case. Even during this month, the average maximum temperature at a depth of 2 inches was higher in carbon-treated soil. As these were the hottest days (air temperature) in the measured periods, the concentration of salts produced by carbon seemed to have the effect of protecting the surface of the soil from extremely high temperatures during drought. The whitening phenomenon might not have occurred if lower rates of fertilizer application had been employed, since lower concentrations of salts would have been in the near-by soil water to come to the surface as the water evaporated. The lowering of the maximum temperatures of carbon-treated soil during this period was due to the loss of heat involved in the high rate of evaporation which brought the salts to the surface on such hot, dry days, and partly to the reflection of light by the whitened surface.

The whitening effect of salt accumulation at the surface of carbon-treated soils did not repeat itself until the hot, moderately dry spell in August, 1947.

Laboratory tests showed (table 3) that carbon-treated soil evaporates more water than does an untreated one. In the field the movement of liquid water to points near the soil surface causes higher salt concentrations when the water evaporates. It is logical to assume then that the whitening of the carbon-treated soil was due to residual salts left by water which had evaporated.

TABLE 3

Evaporation from carbon-treated and untreated soils in sunlight in 1944

DATE	TIME	TEMPERATURE		CUMULATIVE WATER LOSS		
		C-treated soil	Untreated soil	C-treated soil	Untreated soil	Increase in C-treated soil
		°C.	°C.	gm.	gm.	gm.
April 21	9:30 a.m.	20.0	20.0	0	0	0
	1:35 p.m.	24.2	23.4	2.7	1.7	1.0
	3:35 p.m.	27.8	26.8	4.9	3.5	1.4
April 22	9:45 a.m.	27.8	27.8	26.9	24.8	2.1
	11:00 a.m.	32.0	32.0	28.1	24.9	3.2
April 24	9:15 a.m.	22.4	22.0	54.8	49.3	5.5
	2:10 p.m.	24.0	23.0	57.7	52.3	5.4
	4:10 p.m.	23.5	23.0	57.7	52.3	5.4
April 25	9:45 a.m.	22.0	22.0	69.6	63.3	6.3
April 26	9:00 a.m.	25.0	24.0	85.5	78.3	7.2

The phenomenon of salt accumulation cannot be evaluated as entirely beneficial or entirely harmful. It will offset the tendency of rains to carry nutrient salts below the level useful to plants, since the salts are continually returned toward the surface region by the higher evaporation from carbon-treated soils. On the other hand, the very high rates of evaporation occurring during hot spells may carry the salts above the level useful to crops, especially deep-rooted ones. It may increase loss of salts by surface runoff during rain.

WATER-HOLDING CAPACITY OF SOILS

Tests were made by the Hilgard method[6] on the maximum water-holding capacity of carbon-treated (4,000 pounds Elf 3 per acre) and untreated soil. The average maximum water-holding capacity of the carbon-treated Merrimac soil was 54.6 per cent of the sample's dry weight, whereas that of the untreated soil was 45.9 per cent.

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[6] Lyon, T. Y., and Buckman, H. O. Nature and Properties of Soil. Macmillan, New York. 1937.

Similar tests on Cheshire soil, made at the same rate of carbon application using carbon blacks having pH values of 3, 5, and 9, gave the following average maximum water-holding capacities: untreated Cheshire soil, 53.5 per cent; treated with Mogul, pH 3, 60.3 per cent; treated with Elf 3, pH 5, 70.0 per cent; treated with Sterling S, pH 9, 60.0 per cent.

These experiments show that carbon-treated soils can retain more water than untreated soils. As discussed below, the higher energy intake of the carbon-treated soil may result in evaporation of moisture as well as temperature increase.

EFFECT OF MOISTURE ON HEATING AND COOLING OF CARBON-TREATED AND UNTREATED SOILS

Samples of dry Merrimac soils, one treated with 0.1 per cent Elf 3 carbon and the other untreated, in beakers were exposed to the sun's rays for several days. On sunny days, the carbon-treated soil was 1° to 2°F. warmer than the untreated from 10 a.m. to 3 p.m. For a period in the morning and another in the afternoon, both soils were at the same temperature. In early morning and late afternoon, the carbon-treated soil was cooler, even in full sunshine. At night, the carbon-treated soil remained ½°F. cooler than the untreated soil, or else both soils were reduced to air temperature.

A weight of water equal to the dry weight of soil was added to each of the samples. This reduced the maximum temperature of both soils about 4°F. on the average when exposed to conditions similar to those of the dry soils. The maximum temperature of the carbon-treated soil was still above that of the untreated soil, but the difference was not so great as for dry soils. The carbon-treated soil showed greater water evaporation than the untreated soil, as shown below.

One-half of the air-dried sample of Merrimac fine sandy loam was mixed with Sterling S carbon at the rate of 4,000 parts in 500,000. To 250-gm. samples of treated and untreated dry soils in separate beakers, 100 gm. of water was added. Water and soil were both at 20° initially. The beakers were placed in the sun in the laboratory. Table 3 shows temperatures and water losses.

Thus, in 5 days, the carbon-treated sample evaporated 7.2 gm., about 9 per cent, more water than the untreated sample, representing an additional loss of about 4,200 gram-calories. The temperature of the carbon-treated soil was higher than that of the untreated soil in spite of this heat loss. In the field, because new water is constantly supplied from lower soil, greater differences in evaporation may occur.

These experiments show that heat absorbed into soils may be expended by an evaporation of water as well as by raising the temperature level. The carbon-treated soil still absorbs more heat but, since it evaporates more water, its temperature may not be significantly higher than that of the untreated soil.

TIME OF ICE-BAND REMOVAL

During spring, alternate freezing and thawing of the surface soil together with upward movement of water causes ice crystals in a stratum some distance below the surface. Until this ice band has thawed, water may be prevented from percolating downward. The soil is too soggy to plow until this frosty layer thaws. It takes more heat to warm a wet soil than a dry one.

Ice-band removal tests were made in 1945 and 1946 in a flat area of Agawam soil. When the surface was completely saturated with moisture because of the presence of an ice band, insertion of a rod showed solid frost at 12 inches. Part of the soil had been given a surface application of Elf 3 in 1944 and of Sterling S in 1945, both at the rate of 4,000 pounds per acre. Dial thermometers at 6-inch depth showed the temperature remaining at 32°F. until the frost thawed, letting the water pass downward into the soil. In 1945 the carbon-treated soil thawed 2 days earlier than the untreated soil. In 1946 the soil with carbon-treatment thawed 1 week earlier and was dry enough for plowing 2 weeks earlier than the untreated soil. There was less frost in the 1945 soil because of a heavy snow cover.

Before true complete frost removal, the carbon showed another warming effect on the soil. On January 27, 1945, the carbon-treated soil thawed to 2 inches under snow. Untreated soil did not thaw.

These tests showed, for the 2 years tested, an earlier removal of the frost band in carbon-treated soil. During the year of heavier frost, this had a considerable effect on the time at which the soil was dry enough for plowing.

TIME OF SOIL FREEZING

Both carbon-treated and untreated soils were frozen at the surface under the snow December 1, 1944. The untreated soil was frozen to 31°F. at a depth of 2 inches throughout this day. The carbon-treated soil at 2-inch depth was at 32° or lower for only 17 hours. By December 3, the untreated soil was frozen to 12-inch depth for 24 hours. On December 22 the carbon-treated soil froze for the first time to 2-inch depth for 24 hours. During the entire winter the maximum temperatures of the carbon-treated soil were a few degrees higher than those of the untreated soil at 2-inch depth.

This test showed, for the single year studied, a considerable postponement of freezing of soils below the surface where carbon black was applied.

pH OF SOILS

Measurements were made with a Beckman pH meter, using a 1:2 ratio of soil to water. The Merrimac soil used had a pH value of 5.6. The Cheshire soil was at pH 5.7. Soil samples from the field showed that these pH values were not changed by the addition of Elf 3 black, pH 4, or Sterling S black, pH 9, at rates up to 4,000 pounds per acre.

OTHER POSSIBLE EFFECTS

Further studies are needed on other effects of carbon-black on soils. Possible increased retention of ammonium salts by absorption on the carbon should be investigated further. There are also possible effects on retention of other nutrients and trace elements. In 1944 plants were treated with fertilizer containing ammonium sulfate, urea, and cotton seed meal but no nitrates. The carbon plot showed the presence of nitrates in 40 days, whereas the untreated showed no nitrate nitrogen until 50 days after fertilizer application. Darkening soils as a means of producing earlier nitrification should be studied.

A few tests of blacks of different pH seemed to indicate that thin surface application of such a colloid with suitable pH may lessen "damping off." A study is also indicated as to the effects of small additions of colloids on ionic exchange in soils.

DISCUSSION

In the preceding sections clarity of initial presentation has required separate consideration of several effects which are in reality interrelated; this section is included to show the connections believed to exist between the effects noted.

The major effect of the *blackness* of carbon black seems to be a simple one: it increases the energy intake, during the day, and adds slightly to the radiation, during the night, of soils treated with it. Increased energy intake would seem to be the direct cause of several of the results noted. Increased temperature, postponement of freezing in soils, and earlier frost removal probably stem directly from increased energy intake. Increased energy intake is also a requisite for higher moisture evaporation without noticeable cooling of the soil.

Colloidal carbon aggregates some soils and adds new area to the soil interfaces. An application of 1,200 pounds per acre aggregated some soils so that all particles were above the dimensions of clay. This aggregation serves to allow freer passage of moisture through the soil and also makes the soil easier to cultivate. Other results of the alteration of colloidal properties of the soil may include all of the following: increased maximum water-holding capacity, increased average moisture content, increased evaporation, and increased salt accumulation near the surface. It is a paradox that the surface of carbon-treated soil shows a higher moisture content in spite of the fact that more moisture is evaporated from it. No definite reason for this has been presented, although there are several possible theories. These will be considered in a later paper.

SUMMARY AND CONCLUSIONS

A previous paper presented the effects on field soil temperatures of addition to a Merrimac soil in Amherst, Massachusetts, of carbon black at the rate of 2 tons per acre mixed into the top 2 inches (0.7 per cent). The present paper discusses heat and other effects observed when carbon black was added to this and other soils. The same field application caused increases in wet and dry flocculation, in accumulation of salts near soil surfaces, in water-holding capacity, and in moisture content. Some other soils tested showed no aggregation when carbon black was added, and no water-stable aggregation was observed in any soil.

Carbon black, in the proportions used, caused some postponement of soil freezing in fall and advanced time of ice removal from soil in spring. No change of pH was shown. The interrelation of moisture content and temperature in the heating of carbon-treated soils is also discussed.

It is concluded that carbon black, by darkening soils, increases energy absorption, and because of the differences in charges between colloidal clay and carbon, flocculation and an aggregation occur in some soils.

FACTORS DETERMINING EFFICIENCY OF CYANAMID AND URAMON FOR WEED CONTROL IN TOBACCO PLANTBEDS

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Calcium cyanamide and urea are now widely used for killing weeds in tobacco plantbeds. The materials are available as Granular "Aero" Cyanamid and Uramon. They are most commonly used on light sandy soils either singly at the rate of 1 pound per square yard of bed, or in combination of 1 pound of Uramon plus ½ pound of Cyanamid[2] per square yard. Under Florida conditions beds are treated in early October and planted in late December or early January. Clark, Volk, and Stokes (2) have reported generally satisfactory results with all three treatments in sections of the state where flue-cured tobacco is grown, but occasionally failures occur because of lack of weed control or from apparent residual toxicity at the time of planting the tobacco seed. Unsatisfactory results often appeared to be a response to an unusually dry or wet season, possibly further enhanced by certain soil conditions.

The possible reactions through which cyanamide may pass in the soil have been summarized by Buchanan and Barsky (1) and by Crowther and Richardson (3). The normal reaction of moderate amounts of cyanamide in the presence of adequate buffering acidity in moist soil results in the formation of hydrogen cyanamide (H_2CN_2) which hydrolyzes to urea. The latter is then converted to ammonia, presumably by biochemical ammonification. In the alkaline range above pH 8.0, hydrogen cyanamide tends to polymerize to dicyandiamide [$(H_2CN_2)_2$]. Both hydrogen cyanamide and dicyandiamide are known to be toxic to plants, but the latter is thought to be much more stable and persistent in the soil (3, 9). It is also well known that calcium cyanamide and dicyandiamide have a depressing effect on nitrification in the soil, the latter apparently more so than the former (8).

METHODS AND MATERIALS

Soils used in the various tests and the size of field plots and number of replications from which data were averaged are given in table 1. Each plot was sampled by taking 12 plugs 5 inches deep to form a composite. All determinations were made on field-moist samples immediately after collection. Data reported are the average of analyses on moisture-free basis of such samples. All laboratory tests were with Lakeland fine sand-III. Fellowship clay loam is not used for tobacco plantbeds in Florida, but was included in one series of tests to show comparative data for a heavy soil. Erosion had left this soil relatively low in organic matter.

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[1] Soil samples from plantbeds were made available through the cooperation of Fred Clark, assistant agronomist.

[2] In this paper *Cyanamid* is used to designate the commerical product; *cyanamide*, the exact chemical $CaCN_2$.

The Uramon used in the tests was the usual 42 per cent nitrogen material. The Cyanamid used was from freshly opened bags. Table 2 gives analyses of two freshly opened bags of material of different ages. Some decomposition with age is evident, as would be expected (5). A fresh supply of Cyanamid was obtained for each new set of field tests. The laboratory tests were made with freshly opened material 22 weeks after procurement.

Weed control chemicals for field plot tests were broadcast when the soil was moist and were worked into the surface 3 inches. Beds were left uncovered and occasionally received a limited amount of supplemental moisture in addition to rainfall. During dry periods, they had adequate opportunity to become moderately dry. Test plots were treated in early October and tobacco was seeded between December 25 and January 5. In laboratory tests the chemical was thoroughly mixed with the soil and then made up to predetermined field-capacity moisture for any given period of incubation.

TABLE 1

Composition of soils, plot size, and number of replicates used in field tests

SOIL TYPE	pH	ORGANIC MATTER	MOISTURE EQUIVALENT	FIELD PLOT SIZE	NUMBER OF REPLICATES
		per cent	*per cent*	*sq.yd.*	
Lakeland fine sand—I	5.89	0.93	3.1	1.64	3
Lakeland fine sand—II	5.80	1.57	5.3	4.92	2
Lakeland fine sand—III	5.97	1.09	4.0	2.42	2
Archer very fine sand	5.99	2.14	6.4	16.70	2
Hernando fine sand	6.01	1.84	5.2	15.36	2
Fellowship clay loam	5.83	1.55	14.8	12.50	2

TABLE 2

Analysis of cynamid from freshly opened 100-pound bags of different ages

	PERCENTAGE OF NITROGEN		
	Guarantee	1 week*	22 weeks†
Calcium cyanamide	16.12‡	16.20	14.03
Dicyandiamide	Not stated	2.53	4.20
Total nitrogen	20.6	20.14	20.12

* Time held after receipt from American Cynamid Company.

† Time held after procuring from fresh local supply.

‡ Composition stated on the bag as 46 per cent calcium cyanamide and 54 per cent inactive ingredients.

A modification of Matthews' aspiration method (7) involving mechanical shaking of the replacement chamber was devised for determination of ammonia. Methods for hydrogen cyanamide and dicyandiamide were modified to reduce errors introduced by the soluble organic matter present in chemically treated beds. Four hundred grams of moist soil was placed in 400 ml. of water, 1 level tablespoon of precipitated calcium sulfate added, and the suspension shaken 1 hour and filtered. Aliquots of this were then taken for hydrogen cyanamide determination by precipitation as silver cyanamide, and for dicyandiamide determination by the silver-picrate–monocyanoguanidine method proposed by Harger (4) with the following modification: Fifteen ml. of 6 per cent picric acid solution in alcohol was used in place of 100 ml. of 1 per cent water solution of picric acid. The resultant 85 ml. of solution volume saved was substituted with additional soil extract, thereby almost doubling the sensitivity of the method. The use of alcoholic picric acid gave no measurable change in the solubility correction value for the method. Analysis of precipitates obtained from field plot extracts gave total nitrogen values of 22.4 to 22.7 per cent; and from pure dicyandiamide, 22.7 per cent; as against a theoretical 23 per cent based on the formula $C_6H_2(NO_2)_3OAg \cdot C_2H_4N_4$ proposed by Harger.

The extraction procedure accounted for all but 2 ppm. of an application of 280 ppm. of H_2CN_2 nitrogen and 9 ppm. of an application of 123 ppm. of $(H_2CN_2)_2$ nitrogen both applied as concentrated solution to Lakeland fine sand. Silver-picrate–monocyanoguanidine is very soluble in water, whereas the silver-saturated organic matter contamination is not. A corrected value was obtained by washing the silver-picrate–monocyanoguanidine through the crucible with copious amounts of water and obtaining its true weight by difference.

TABLE 3

*Change in soil pH following repeated annual use of cyanamid and uramon for weed control on Lakeland fine sand-I**

TREATMENT PER SQUARE YARD	SOIL pH			
	Initial composite, Oct., 1945	Oct., 1946	Oct., 1947	Oct., 1948
1 lb. Uramon	5.89	6.63	6.51	6.72
1 lb. Cyanamid	5.89	7.68	8.03	7.85
1 lb. Uramon plus ½ lb. Cyanamid	5.89	7.28	7.77	7.78
Check	5.89	6.18	6.06	6.37

* Samples were taken just before treatment each fall.

RESULTS

Effect of treatment on soil pH, ammonia, nitrates, and nitrites

Repeated annual applications of Uramon and Cyanamid singly and in combination to plantbeds on Lakeland fine sand-I all resulted in an increased soil pH, as shown in table 3.

Maximum effective pH apparently was reached in two annual treatments. Plantbed fertilizer probably had some effect, as shown by the check. The pH change from the time of the second annual treatment in October of 1946 until seeding time is shown in figure 1. The fact that the pH following Uramon alone drops rapidly back toward neutral, whereas the pH following Uramon plus only

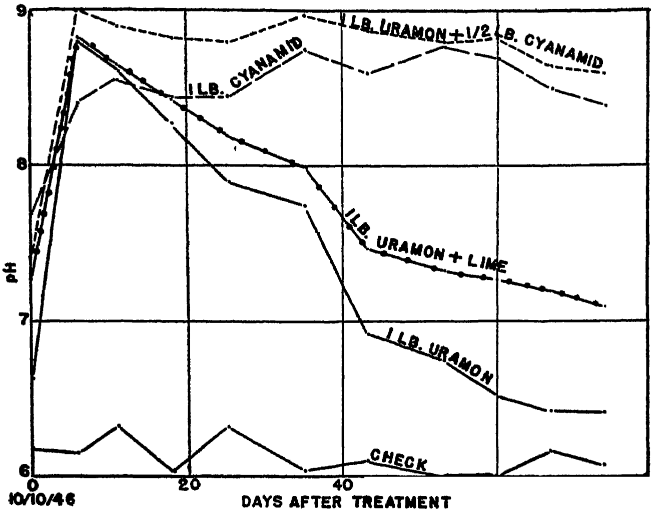

FIG. 1. pH CHANGES IN LAKELAND FINE SAND FOLLOWING THE SECOND ANNUAL APPLICATION OF WEED CONTROL CHEMICALS

Application rates per square yard

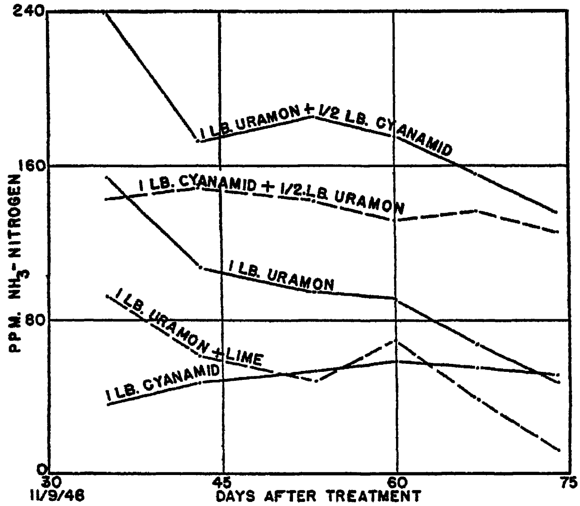

FIG. 2. AMMONIA NITROGEN IN LAKELAND FINE SAND AFTER TREATMENT WITH WEED CONTROL CHEMICALS

Application rates per square yard

½ pound of Cyanamid holds above that following a full pound of Cyanamid, suggests that the retarding effect of Cyanamid on nitrification of ammonia from the Uramon is a factor over and above the alkalinity supplied by the Cyanamid.

Figure 2, showing the levels of ammonia between the 35th and 74th days, and figure 3, giving the buildup of nitrates, substantiate the foregoing conclusion.

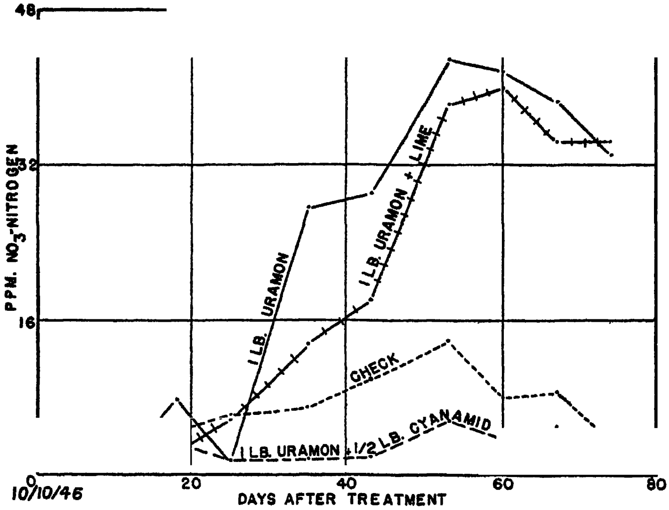

FIG. 3. NITRATE NITROGEN IN LAKELAND FINE SAND AFTER TREATMENT WITH WEED CONTROL CHEMICALS

Application rates per square yard

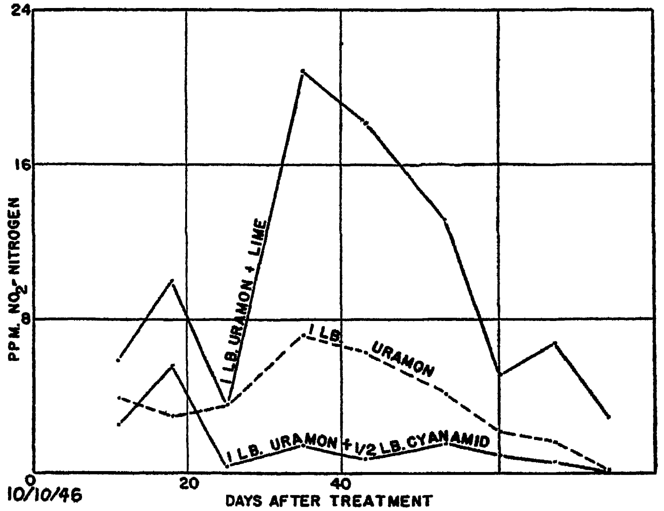

FIG. 4. NITRITE NITROGEN IN LAKELAND FINE SAND AFTER TREATMENT WITH WEED CONTROL CHEMICALS

Application rates per square yard

Cyanamid retarded nitrification to some extent for the entire 74 days. In the absence of Cyanamid, nitrification accelerated rapidly beginning about the 20th day after treatment. Prior to this time the high pH resulting from the ammonia apparently retarded nitrification even in the absence of Cyanamid, as shown by figure 3. The explanation probably lies in data given by figure 4 on the buildup of nitrites in Uramon and Uramon plus lime treatments. The so-called "threshold" pH of 7.7 established by Martin *et al.* (6) was exceeded, suggesting that high pH was the reason that conversion of ammonia stopped at the nitrite stage, probably as a result of partial sterilization or inactivation with respect to nitrate-forming organisms.

It is of interest to note that nitrites did not form in significant quantity from Uramon when Cyanamid was present, indicating that the latter was inhibiting to nitrite-formers. Possibly this is a limiting function of Cyanamid in the retardation of nitrification previously mentioned, if formation of nitrites is considered as an essential step in conversion of ammonia to nitrates. Tobacco seedling injury attributed to high nitrite nitrogen found to be present has been noted at times following the use of Uramon in the weed control treatment.

Persistence of hydrogen cyanamide and dicyandiamide in the soil

Data in table 4 were obtained from first season treatments carrying Cyanamid, except those for Fellowship clay loam, which were taken following the third annual treatment, and those from one test on Lakeland fine sand-I, which followed the fourth annual treatment. The amount of dicyandiamide found in the Lakeland fine sand-I, 32 days after treatment, averages 60 per cent of the original nitrogen applied in the 1 pound of Cyanamid per square yard based on a 5-inch depth of sample[3]. The original material carried dicyandiamide nitrogen of about 2.53 per cent and calcium cyanamide nitrogen of 16.2 per cent according to analysis of similar fresh material (table 2), therefore it is assumed that up to 61 per cent of the applied calcium cyanamide nitrogen was accounted for as dicyandiamide nitrogen 32 days after applicatoin. The relative amount held in the clay loam was still higher but is assumed to be a function of reduced leaching rather than greater initial formation. The amount remaining from the combination of 1 pound of Uramon with ½ pound of Cyanamid was significant only in Fellowship clay loam and Lakeland fine sand-I. The difference between the first and fourth year tests on the latter soil correlates with soil pH and may be a response to its effect on dicyandiamide formation.

Up to 54 ppm. of dicyandiamide nitrogen was still present in the light soils at planting time 87 days after treatment. Leaching undoubtedly plays a dominant role in removal of toxic residues, especially in the case of the dicyandiamide which tends to resist decomposition for such an extended period. It is evident that given the proper conditions of pH, soil type, and dry weather, sufficient dicyandiamide could persist to be a factor in germination of tobacco seed. The bed on Archer very fine sand showed evidence of toxicity assumed to be dicyandiamide injury.

Because of the known influence of factors such as poor distribution of Cyanamid, excessive drying, and leaching in field plantbeds, it was thought desirable to determine the rate and type of decomposition of high amounts of Cyanamid in soil under controlled conditions. Granular Cyanamid from freshly opened bags 22 weeks after procurement was added at rates of 0.5, 1.0, and 1.5 gm. to

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[3] Lakeland fine sand has been measured at 1,040 tons per acre 6 inches.

TABLE 4

Persistence of dicyandiamide and hydrogen cyanamide in field plantbeds

Treated October 11, 1948. One pound of Cyanamid per square yard approximates 576 ppm. nitrogen per acre 5 inches of Lakeland fine sand.

SOIL TYPE	YEAR OF TREATMENT	SOIL pH Oct. 11, 1948	1 LB. CYANAMID PER SQUARE YARD				½ LB. CYANAMID PLUS 1 LB. URAMON PER SQUARE YARD			
			H_2CN_2 as ppm.-N	$(H_2CN_2)_2$ as ppm.-N			H_2CN_2 as ppm.-N	$(H_2CN_2)_2$ as ppm.-N		
			Nov. 12, 1948	Nov. 12, 1948	Dec. 3, 1948	Jan. 6, 1949	Nov. 12, 1948	Nov. 12, 1948	Dec. 3, 1948	Jan. 6, 1949
Archer very fine sand	1st	5.99	0	263	189	54	0	7		
Lakeland fine sand—II	1st	5.80	0	185	19	0	0	4		
Hernando fine sand	1st	6.01	0	250	23	11	0	5		
Lakeland fine sand—I	1st*	6.73	36	360	225	31	17	59	40	0
Fellowship clay loam	3rd	6.70	32	442	435	125	12	143	87	23
Lakeland fine sand—I	4th	7.49	17	329	233	26	27	113	87	11

* These beds had been used before but not with Cyanamid. The pH was raised by previous fertilization.

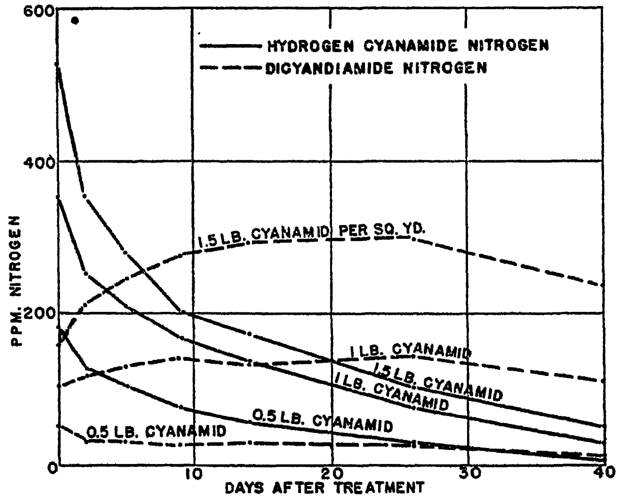


FIG. 5. DECOMPOSITION OF CALCIUM CYANAMIDE AND FORMATION AND DECOMPOSITION OF DICYANDIAMIDE IN LAKELAND FINE SAND AT FIELD-CAPACITY MOISTURE IN LABORATORY TESTS

Rates are approximate field applications per square yard. See text for exact weight ratio.

400 gm. of Lakeland fine sand-III at field capacity, and allowed to incubate at room temperature. Samples were removed after various time intervals and analyzed for H_2CN_2 and $(H_2CN_2)_2$. Results are presented in figure 5. Initial points at 0 time represent the amounts present in the material added.

There was a rapid initial drop in cyanamide in 10 days, and cyanamide had largely disappeared in 40 days. Dicyandiamide, however, increased where the 1.5-gm. application had been made. By the end of 20 days, it had about doubled and at 40 days it was still considerably above the original amount. The intermediate quantity was back about to an equivalent of that added, while the lowest quantity had gone through a more or less constant decrease.

Figure 6 summarizes the results in figure 5 to show an important relationship thought to be a factor of granulation of Cyanamid. After the initial drop of total H_2CN_2 plus $(H_2CN_2)_2$ during about the first 15 days, the slopes of the curves are about parallel. This shows that further disappearance of the combined materials was probably a function of the original number of granules and that it was of approximately equal rate per unit of surface area. Horizontal displacement of the curves indicated that less cyanamide plus dicyandiamide was left in granules of lower application levels as a result of an initially different rate of disappearance until the fifteenth day, but that thereafter the granule crust had become uniform for all levels of application and thence diffusion of soluble material through it was uniform and proceeded as described above after the fifteenth day (10). The fact that these data were obtained on soil probably ideally moist for normal hydrolysis of cyanamide to urea and that the ratio of Cyanamid to soil would represent ideal mixing must be considered. Under field conditions, poorer distribution both in depth and completeness and the effect of periodic drying of cyanamide granules near the surface could easily halve the critical amount applied to give the same results (10).

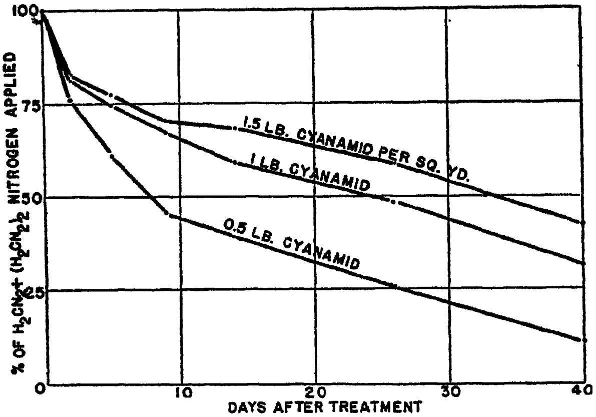
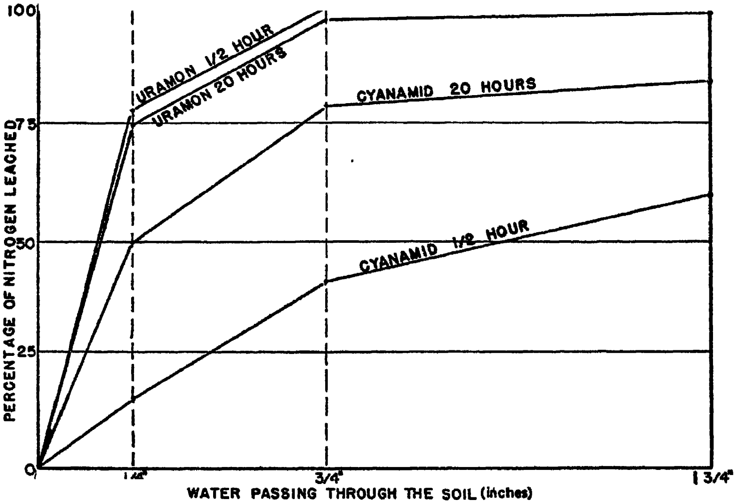


FIG. 6. RATE OF DISAPPEARANCE OF CYANAMIDE PLUS DICYANDIAMIDE NITROGEN FROM LAKELAND FINE SAND AT FIELD-CAPACITY MOISTURE IN IN LABORATORY TESTS

Rates are approximate field applications per square yard. See text for exact weight ratio.

Effect of leaching on efficiency of weed control

It had been noted that moderately heavy rains within a day or two after treatment could render Uramon ineffective in killing weed seeds but did not materially affect Cyanamid. To examine this factor, 1-pound rates of Cyanamid and Uramon, singly, and in combination of 1 pound plus ½ pound, respectively, were applied in duplicate to field plots and incorporated in the usual manner. Soil samples were taken immediately. The intention was to add a measured amount of water to determine its effect on movement of the chemicals, but 1.6 inches of rain fell within the next 2 hours. Soil samples were taken the next day when it was assumed that the surface soil had reached field capacity. Both these and pre-rainfall samples were analyzed for total nitrogen. After deduction of a soil blank, data showed that 85 per cent of the Uramon nitrogen had disappeared from the surface 6 inches of soil while only 48 per cent of the Cyanamid had disappeared. Weed control was good where Cyanamid alone or in combination had been used, but Uramon alone gave no weed control.



IG. 7. COMPARATIVE RATES OF LEACHING OF NITROGEN FROM LAKELAND FINE SAND FOLLOWING APPLICATION OF 0.5 GM. OF URAMON OR CYANAMID TO 200 GM. OF SOIL AFTER STANDING ½ HOUR OR 20 HOURS AT FIELD-CAPACITY MOISTURE

Better controlled laboratory tests were made by adding the equivalent of 0.5 gm. of Uramon or Cyanamid to 200 gm. of soil in a 4½-inch Büchner funnel and making up to field-capacity moisture for incubation at room temperature. In one set of tests the incubation was allowed to proceed for ½ hour; in another, it was allowed 20 hours. The funnels were then leached with aliquots of water equal to ¼ inch, ½ inch, and 1 inch in succession, a total of 1¾ inches through a given funnel. Each funnel was sucked free of any water that would immediately come through the soil. Thirty minutes was allowed for each aliquot to soak the soil before the suction was applied. Results on total nitrogen less a soil extract blank appear in figure 7.

The test is entirely arbitrary but serves to show the difference in mobility of the materials in soil. Uramon was readily soluble and its removal dependent apparently only on the degree of replacement of the soil solution. The drop in total nitrogen obtained from the Uramon treatment after 20 hours could be attributed to partial conversion to ammonia and retention in that form. Data on the Cyanamid show that mobility is much less at ½ hour than at 20 hours, indicating that the rate of solubility of the granular material is probably the factor involved. The results in general substantiate field observations that rainfall sufficient to remove virtually all of the Uramon immediately after application would move approximately one half of an equal weight of Cyanamid.

The relative ease with which materials may be leached enhances the value of speed of seed kill following application. Table 5 presents results obtained on millet, radish, and mustard seeds used as a measure of relative effectiveness. Seeds were placed in filter paper envelopes and embedded in beakers of soil, at field capacity, carrying the various chemicals mixed through it at a weight-ratio approximating field application incorporated to a 3-inch depth. They were removed after 2 and 5 days and germination tests made at room temperature.

TABLE 5

Effectiveness of cyanamid and uramon in killing weed seeds in Lakeland fine sand at 60°F. Results are from duplicate tests of 50 seeds each

TREATMENT PER 400 GM. SOIL	2-DAY TREATMENT						5-DAY TREATMENT					
	Germination 24 hr. at 78°F.			Germination 72 hr. at 78°F.			Germination 24 hr. at 78°F.			Germination 72 hr. at 78°F.		
	Millet	Mustard	Radish	Millet	Mustard	Radish	Millet	Mustard	Raddish	Millet	Mustard	Radish
	%	%	%	%	%	%	%	%	%	%	%	%
2 gm. Cyanamid	0	1	1	2	10	28	0	0	0	1	0	0
2 gm. Uramon	79	74	97	75	85	98	0	0	1	0	0	1
2 gm. Uramon plus 1 gm. Cyanamid	1	2	9	7	5	47	0	0	0	0	0	0
None	81	70	98	81	77	98	67	75	98	67	77	99

Cyanamid was readily effective. Crowther and Richardson (3) report that penetration of the seed by the CN_2 ion is all that is necessary, changes attending germination being unessential. Uramon, however, was not effective when left in contact 2 days, but seed left in contact 5 days were effectively killed. On the assumption that ammonia was the killing agent in the Uramon treatment, 5 days probably represented the time necessary for its effective accumulation from the conversion of urea. Urea itself, absorbed by the seed in 2 days, apparently was not effective in killing the seed.

If ammonia is the effective agent as indicated, then factors such as soil temperature and pH might be significant, the latter especially so if free ammonia is more effective than that combined with the exchange complex or strong anions. The temperature of Lakeland fine sand at the 4-inch depth at Gainesville varies from about 82°F. on October 1 to 58°F. on January 1, the period covering the weed control treatment. It fluctuates as much as 20 degrees between night minimum and day maximum and usually shows at least half the fluctuation noted for air temperatures during a given 24-hour period[4].

A test in which ammonia evolved at various temperatures was measured without air movement over the soil was made by adding 0.23 gm. of Uramon to 100 gm. of Lakeland fine sand at field-capacity moisture in pint Mason jars and absorbing evolved ammonia in 10 per cent H_2SO_4 on glass wool in a crucible placed

TABLE 6

Effect of temperatures on rate of conversion of Uramon and evolution of NH_3 *following addition of 0.23 gm. of Uramon to 100 gm. of Lakeland fine sand*

Results are averages of duplicate tests using absorbers consisting of 10 per cent H_2SO_4 in crucibles on soil in pint Mason jars with rubber rings but unsealed.

	TIME	58°F.	79°F.	90°F.
	hours			
pH of soil not air-dried	12	5.81	8.32	8.48
	36	8.62	8.92	8.92
	60	8.91	9.05	9.00
	84	8.92	8.96	8.86
	156	8.99	8.90	8.78
Evolved NH_3-nitrogen, percentage of application	12	0.0	0.1	0.1
	36	0.1	1.2	3.4
	60	0.5	8.7	20.3
	84	3.1	23.1	36.9
	156	25.5	43.6	55.8
NH_3-nitrogen held by moist soil, percentage of application	12	5.5	9.8	14.3
	36	16.6	34.2	45.3
	60	28.5	58.8	68.5
	84	46.5	65.7	57.8
	156	67.0	56.1	43.6
NH_3-nitrogen held by air-dry soil, percentage of application	12	—	—	—
	36	15.9	26.5	29.6
	60	22.9	32.3	37.2
	84	31.3	35.4	37.0
	156	49.5	42.5	34.4
Percentage of application not accounted for as NH_3	12	94.5	90.1	85.6
	36	83.3	64.6	51.3
	60	71.0	32.5	11.2
	84	50.2	11.2	5.3
	156	7.5	0.3	0.6

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[4] Data obtained by the U. S. Department of Agriculture Tung Laboratory, Gainesville, Florida.

in the jar. The jars were closed with rubber rings and glass tops but not sealed. Temperatures of 58, 79, and 90°F. were used. The test was conducted so that duplicate jars could be removed for analysis at each time interval for each temperature. Results are reported in table 6.

The maximum soil pH reached was about 9.0 for any temperature. This dropped to about 8.6 on air-drying. Evolved ammonia showed an approximate correlation of 60 hours for 90°, 84 hours for 79°, and 156 hours for 58°. Ammonia held by the moist soil at these times was at a maximum and was approximately equal for each temperature, showing that high rate of evolution at high temperatures is the result of rate of decomposition rather than accelerated rate of evolution from otherwise equivalent decomposition. Ammonia nitrogen in the soil at the end of the 156-hour period plus that evolved accounted for 92.5, 99.7, and 99.4 per cent of total applied nitrogen for low to high temperatures, respectively. The ammonia level after air-drying of the soil supports the contention that ammonia replaces calcium in the exchange complex as calcium is precipitated by CO_2. At the high temperatures ammonium carbonate would be more rapidly decomposed and CO_2 and NH_3 more readily volatilized, therefore less effective in precipitating calcium from the exchange complex.

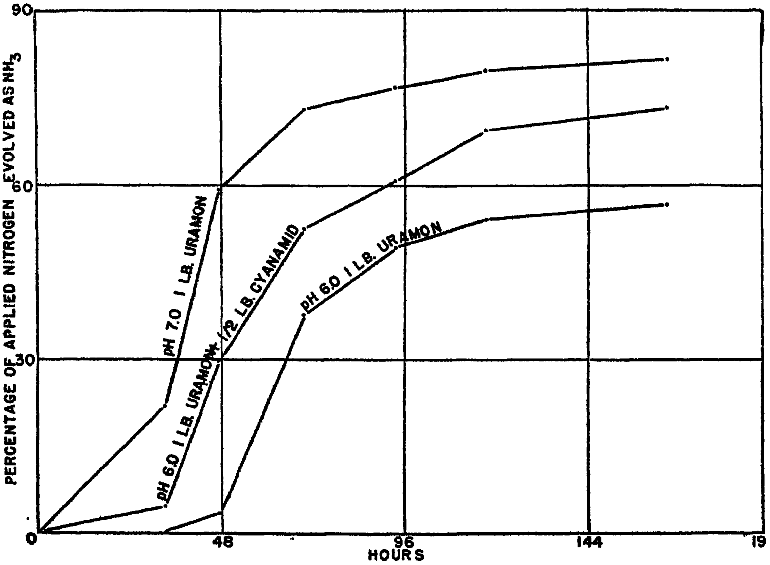

FIG. 8. EFFECT OF SOIL PH AND CYANAMID ON PRODUCTION AND EVOLUTION OF AMMONIA FROM 0.23 GM. URAMON IN 100 GM. LAKELAND FINE SAND AT FIELD-CAPACITY MOISTURE

Figure 8 shows the rate of evolution of ammonia at room temperature from Uramon applied to Lakeland fine sand-III at pH 6.0 and 7.0, and from a combination of Uramon and Cyanamid on soil at pH 6.0. Uramon was applied at the rate of 0.23 gm. to 100 gm. of soil and Cyanamid at half this rate. The soil was selected from a series of plots previously limed in the field to produce the different pH values. Incubation was carried out in 300-ml. Erlenmeyer flasks through which was slowly drawn ammonia-free air brought to equivalent temperature and saturated with moisture. Evolved ammonia was absorbed in a bead column of standard acid. The lower evolution at pH 6.0 could be almost entirely accounted for by ammonia found to be retained in the soil at pH 6.0 as compared to pH 7.0. The ammonia evolved plus that residual in the soil at the end of the test period, expressed as percentage of application, was 93.2, 102.7, and 99.9 for the pH 6.0 Uramon, pH 6.0 combination, and pH 7.0 Uramon treatments, respectively. Only 6.7 per cent might be attributed to increased biochemical activity brought about by raising the pH.

The increased evolution of ammonia from the combination treatment as compared to Uramon alone is probably a similar function of the alkalinity supplied by the Cyanamid. Cyanamid did not inactivate the breakdown of urea, nor did total ammonia figures indicate significant contribution from its own decomposition.

SUMMARY AND CONCLUSIONS

Repeated use of ½ pound or more of Cyanamid per square yard in weed control treatment for tobacco plantbeds on light sandy acid soils resulted in residual pH values of 7.8 to 8.0. A pound of Uramon alone increased the pH sufficiently above the threshold value of 7.7 to inhibit rapid nitrate-nitrogen production but permitted formation and accumulation of nitrite nitrogen. A pound of Uramon plus ½ pound of calcic lime permitted accumulation of 21 ppm. of nitrite nitrogen 35 days after treatment. When Cyanamid was added to the Uramon, formation of nitrites was inhibited and ammonia and pH remained high for at least 74 days.

Up to 61 per cent of the calcium cyanamide nitrogen in a pound application of Cyanamid was accounted for as dicyandiamide nitrogen 32 days after treatment, and 28 ppm. was still present 87 days after treatment in Lakeland fine sand. Repeated use of this amount of Cyanamid apparently did not enhance the amount of dicyandiamide formed, but annual repetition of the combination treatment carrying only half this amount of Cyanamid apparently did build up the pH and increase the formation of dicyandiamide over that of the first year, when the quantity formed was not significant for acid soils. Hydrogen cyanamide did not persist in measurable quantity after about the first month in any instance.

Determination of the rate of formation and decomposition of dicyandiamide under ideal conditions of mixing with Lakeland fine sand at field-capacity moisture in the laboratory showed a build-up of dicyandiamide nitrogen from heavy applications but not of the magnitude observed in the field where the usual practice introduced poor control of these factors. Latent removal of cyanamide and dicyandiamide appeared to be a function of rate of diffusion out of the Cyanamid granule rather than state of conversion or absorption by the soil itself.

Uramon was found to be so readily soluble and mobile in the soil that a given rainfall should be expected to remove it to the extent that the soil solution would be displaced. Rainfall sufficient to remove virtually all the Uramon would be expected to move approximately half of an equal application of Cyanamid. This largely explained the lack of efficiency of Uramon when rains followed immediately after treatment.

Cyanamid, upon absorption, was immediately effective in killing certain seeds, but Uramon apparently was ineffective until a significant amount had been converted to ammonia, a process apparently requiring more than 2 but less than 5 days at approximate fall soil temperatures. Soil temperature was found to have a marked effect on the rate of decomposition of urea; the higher the temperature, the greater the rate of ammonification.

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MAINTENANCE OF SOIL ORGANIC MATTER: II. LOSSES OF CARBON AND NITROGEN FROM YOUNG AND MATURE PLANT MATERIALS DURING DECOMPOSITION IN SOIL

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It is well known that when young succulent plant materials are incorporated into a soil they decompose rapidly and release a considerable portion of their nitrogen within a few days. In contrast, when mature woody materials are added to a soil they decompose more slowly and commonly retard crop growth unless supplemental nitrogen is applied. These facts have led many to believe that green manure carbon is so readily lost from soil that its addition, although of marked immediate benefit, is of little value in the maintenance of soil organic matter. In the previous paper (2) of the present series data were presented which show that green manure carbon is often held almost as tenaciously as is the carbon from brown manures. A year after incorporation of green oats into soil or sand-colloid mixtures an average of 34 per cent of the carbon remained; where wheat straw plus urea to give the same carbon-nitrogen ratio was added, 38 per cent of the carbon remained. The corresponding figures for the carbon of green soybean plants and corn stover plus urea were 28 and 38 per cent, respectively The present paper reports additional experimental work similar in many respects to that just mentioned and supplemental to it.

The primary purposes of the work reported here were (*a*) to obtain further direct comparisons of the stability, or persistence, of the carbon of green manures with that of mature materials when used as humus[2] sources, and (*b*) to determine to what extent nitrogen additions made to crop residues of wide carbon-nitrogen ratios tend to hold the carbon from these residues in the soil, as some workers (1, 5, 10, 12, 14) have reported or inferred. In addition, information was desired on the magnitude of the nitrogen gains through biological fixation, and on gaseous losses of nitrogen following addition of the various types of plant materials. Comparatively few data are available from long-time, carefully planned experiments that deal with these phases of humus formation.

EXPERIMENTAL METHODS

The methods used were, with minor exceptions, the same as given in the preceding paper (2). The composition of the organic materials used is given in table 1. They were added in sufficient quantities to supply 1 per cent carbon in all cases. All tests were made in beakers at 28°C. in the same Cecil clay loam subsoil (6–14 inches) used previously. This soil had a pH value of 4.9. The rate of application of calcium carbonate, where used, was 0.5 per cent. Urea was added in some instances together with the organic materials in amounts sufficient to make the carbon-nitrogen ratio 10. The soils were maintained at optimum moisture content and were not stirred during the experiment. Each analysis represented a soil from a different beaker rather than one of several samplings from the same beaker. At the end of the incubation period the soils were air-dried, ground in a ball mill, and analyzed for total carbon by the wet combustion method previously described (2). Nitrogen analyses were made by the Kjeldahl method using salicylic acid to include nitrates. All soil treatments were made in duplicate with single analyses for each sample.

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[2] The term "humus" is used to designate the well-decomposed portion of organic matter that has largely lost its original structure.

TABLE 1

Composition of organic materials

MATERIAL	CARBON	NITROGEN	C/N RATIO	LIGNIN
	per cent	*per cent*		*per cent*
Casein	47.9	15.6	3.1	—
Bluegrass	41.7	4.3	9.7	5.3
Oats	39.3	3.7	10.6	4.9
Millet, young	39.4	3.7	10.7	6.3
Soybeans	42.6	2.8	15.0	9.7
Lespedeza	44.3	2.5	18.1	14.2
Millet, intermediate	43.3	1.3	34.1	11.0
Oak leaves	46.3	0.7	64.3	21.9
Wheat straw	43.1	0.6	73.0	16.4
Corn stover	44.0	0.4	102.4	15.1
Cellulose	44.4	—	—	—

RESULTS

Humus formation from succulent green plant materials in acid Cecil clay loam

Table 2 shows the percentages of the added green manure carbon remaining in the soil after varying periods. Five young plant materials were used, three of which were especially succulent. Soybeans and lespedeza were slightly more fibrous than were bluegrass, oats, and millet but were typical green manure crops. When harvested, the soybeans were just starting to form pods and the lespedeza was in the blossom stage. A protein, casein, was included for comparison.

At the end of 1.5, 4, and 12 months of decomposition of the five plant materials in the soil the green manure carbon remaining averaged approximately 49, 40, and 36 per cent, respectively. The corresponding average values for the three most succulent materials were 48, 39, and 33 per cent. The values for casein, namely 25, 17, and 15 per cent, were lower but yet relatively high in view of the rate at which this protein is known to decompose apart from soil and the fact that it contains no lignin or lignin degradation products so important in humus formation. Neither these nor the earlier findings (2) indicate that green manure carbon disappears from a soil as quickly and completely as is generally believed.

Humus formation from mature plant materials in acid Cecil clay loam with and without fertilizer nitrogen

The results of studies similar to those reported in table 2 but with more woody plant materials are reported in table 3. The materials include millet, which was nearly mature, oak leaves, wheat straw, and corn stover. Cellulose in the form of ground filter paper was included for comparison. Since most of these materials were markedly deficient in nitrogen, sufficient fertilizer nitrogen was added to one set of samples to make the carbon-nitrogen ratio of added materials 10. This quantity of nitrogen was known to be much in excess of that required for a maximum rate of decomposition but was used in order to make the results comparable with those of some of the earlier workers. A nitrogen content of 1.2 to 1.5 per cent, which corresponds to a carbon-nitrogen ratio of about 28 to 35, is adequate (7) for a near-maximum rate of humification of crop residues. By use of urea as the nitrogen source, toxic residues were avoided and likewise any danger from excess nitrogen. Urea quickly goes to ammonia, which is readily used by microorganisms, or if formed in excessive amounts, some of it may escape as gas, especially in a limed soil.

TABLE 2

Organic carbon retention in unlimed Cecil clay loam following addition of 1 per cent carbon in the form of succulent green manures or protein

TREATMENT	C/N RATIO OF ADDED MATERIALS	CARBON PRESENT AFTER					
		1.5 months		4 months		12 months	
		Total C	Added C*	Total C	Added C*	Total C	Added C*
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
None		.427		.424		.403	
Casein	3.1	.677	25.0	.598	17.4	.556	15.2
Bluegrass clippings	9.7	.909	48.2	.819	39.5	.745	34.2
Oats	10.6	.900	47.3	.801	37.7	.732	32.9
Millet	10.7	.913	48.6	.826	40.2	.732	32.9
Soybeans	15.0	.895	46.8	.820	39.6	.779	37.6
Lespedeza	18.1	.986	55.9	.867	44.3	.812	40.9

* Portion of added organic carbon remaining. The difference required for significance between these treatment means is 3.7 at the 5 per cent level and 5.0 at the 1 per cent level.

In considering the data in table 3 and in one of the later tables (table 5), one should bear in mind that the figures show the percentages of the added carbon remaining after various incubation periods. It is not to be inferred that this carbon is all humus carbon. As pointed out in the previous paper, the methods for determining humus carbon are so unsatisfactory that it seemed best to determine total residual carbon only. In many cases, such as where a green manure crop has been allowed to decompose for 6 months or longer under optimum conditions, it is safe to assume that virtually all of the residual carbon is well humified. Likewise, more fibrous materials, such as straw, should be rather thoroughly humified after a year if adequate combined nitrogen to permit maximum biological action was supplied. Without the extra nitrogen, however, the crop residue may still be present in only a partly decomposed state.

Table 3 shows that the percentage of the carbon added as millet, wheat straw, and corn stover that remained after 1.5, 4, and 12 months averaged 68, 59, and 47, respectively, where no urea was supplied; where an abundance of supplemental nitrogen was added the corresponding figures were 48, 42, and 38. If oak leaves and cellulose, which are not typical of crop residues, are included the average values for the three periods in the absence of nitrogen are 75, 64, and 54; where urea was present the averages are 53, 45, and 40. These data show that addition of fertilizer nitrogen to carbonaceous crop residues incorporated into the soil is not necessary to hold the maximum amount of carbon. If nitrogen is added, the decay processes are accelerated, as has frequently been shown, and humus formation is favored. The results show that where nitrogen is deficient there is no excessive loss of carbon dioxide; on the contrary, the plant materials tend to remain in a partly decomposed state. From the practical standpoint, there are many good reasons for applying supplemental nitrogen when materials of wide carbon-nitrogen ratio are turned under, especially if a crop is to be planted soon, but to add fertilizer nitrogen for the sole purpose of holding the added carbon would appear from these data to be a practice without scientific basis.

TABLE 3

Organic carbon retention in unlimed Cecil clay loam following addition of 1 per cent carbon in the form of mature (or nearly mature) plant materials and with or without supplemental nitrogen

TREATMENT	C/N RATIO OF ADDED MATERIALS	CARBON PRESENT AFTER					
		1.5 months		4 months		12 months	
		Total C	Added C*	Total C	Added C*	Total C	Added C*
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
None		0.427		0.424		0.403	
Millet, heads formed	34.1	0.977	55.0	0.901	47.7	0.798	39.5
Millet + urea	10.0	0.916	48.9	0.858	43.4	0.790	38.7
Oak leaves	64.3	1.206	77.9	1.117	69.3	0.948	54.5
Oak leaves + urea	10.0	1.082	65.5	1.011	58.7	0.917	51.4
Wheat straw	73.0	1.193	76.6	1.062	63.8	0.920	51.7
Wheat straw + urea	10.0	0.931	50.4	0.847	42.3	0.783	38.0
Corn stover	102.4	1.157	73.0	1.064	64.0	0.890	48.7
Corn stover + urea	10.0	0.875	44.8	0.827	40.3	0.777	37.4
Cellulose	—	1.346	91.9	1.157	73.3	1.178	77.5
Cellulose + urea	10.0	0.990	56.3	0.800	37.6	0.726	32.3

* Portion of added organic carbon remaining. The difference required for significance between these treatment means is 4.8 at the 5 per cent level and 6.4 at the 1 per cent level.

In the presence of urea the percentages of the added carbon remaining after a year were for oak leaves 51, millet 39, wheat straw 38, corn stover 37, and cellulose 32. Most of the carbon loss occurred during the first 6 weeks but after the readily decomposable materials had been utilized, humification proceeded very slowly. The average value of 38 for the three typical carbonaceous plant materials is only slightly higher than the value of 36 reported in table 2 for the five succulent materials (or 33 for the three very young green crops). These values agree closely with those presented in the previous paper of this series. Per unit of carbon added, most succulent green manures seem to furnish carbon that is about 80 to 90 per cent as permanent in the soil as is mature plant carbon. In both cases a considerable, but unknown, portion of the added plant carbon is transformed into microbial carbon. When it is in this form, its resistance to decay would, of course, be largely independent of the nature of the material from which it was derived.

TABLE 4

Organic carbon retention in limed Cecil clay loam following addition of 1 per cent carbon in the form of succulent green manures or protein

TREATMENT	C/N RATIO OF ADDED MATERIALS	CARBON PRESENT AFTER					
		1.5 months		4 months		12 months	
		Total C	Added C*	Total C	Added C*	Total C	Added C*
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
None		.383		.373		.355	
Casein	3.1	.655	27.2	.572	19.9	.551	19.6
Bluegrass clippings	9.7	.789	40.6	.765	39.2	.647	29.2
Oats	10.6	.850	46.7	.785	41.2	.672	31.7
Millet, young	10.7	.801	41.8	.776	40.3	.691	33.6
Soybeans	15.0	.825	44.2	.801	42.8	.690	33.5
Lespedeza	18.1	.868	48.5	.851	47.8	.727	37.2

* Portion of added organic carbon remaining. The difference required for significance between these treatment means is 3.7 at the 5 per cent level and 5.0 at the 1 per cent level.

Humus formation from succulent green plant materials in limed Cecil clay loam

It is a well-known fact that additions of lime to an acid soil usually accelerate the decomposition of added organic materials. Less is known about the effect of lime on the percentage of carbon remaining after several months. The studies with Mohave clay loam, reported in the previous paper of this series, showed that lime usually somewhat increased the loss of carbon at all three incubation periods. Figures for the retention of the carbon of several green crops, allowed to decompose in limed Cecil soil, are reported in table 4. These results are directly comparable with those in table 2 for the unlimed Cecil soil.

The rate of carbon dioxide evolution from the various materials in Cecil soil was, in most instances, increased, but not markedly, by additions of calcium carbonate. At the end of a year the average percentage of the carbon retained, exclusive of that in casein, was about 36 in the absence and 33 in the presence of calcium carbonate. Obviously green manure carbon is a good source of humus carbon regardless of the base content of the soil.

Humus formation from mature plant materials in limed Cecil clay loam with and without fertilizer nitrogen

The effect of lime on the humification of mature plant materials can be seen by comparing table 5 with table 3.

Lime, in most cases, significantly increased the carbon loss, the effect being more marked with increase in length of the incubation period. After a year the approximate average carbon retention figures for the five carbon sources that decomposed under conditions of adequate nitrogen were 38 in the acid soil and 33 in the presence of lime. The effect of lime in accelerating the humification process was, therefore, similar for succulent and mature plant materials but slightly more marked for the latter.

TABLE 5

Organic carbon retention in limed Cecil clay loam following addition of 1 per cent carbon in the form of mature (or nearly mature) plant materials and with or without supplemental nitrogen

TREATMENT	C/N RATIO OF ADDED MATERIALS	CARBON PRESENT AFTER					
		1.5 months		4 months		12 months	
		Total C	Added C*	Total C	Added C*	Total C	Added C*
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
None		0.383		0.373		0.355	
Millet, head formed	34.1	0.902	51.9	0.834	46.1	0.690	33.5
Millet + urea	10.0	0.873	49.0	0.803	43.0	0.692	33.7
Oak leaves	64.3	1.038	65.5	0.971	59.8	0.746	39.1
Oak leaves + urea	10.0	0.957	57.4	0.938	56.5	0.773	41.8
Wheat straw	73.0	1.078	69.5	0.986	61.3	0.752	39.7
Wheat straw + urea	10.0	0.853	47.0	0.816	44.3	0.710	35.5
Corn stover	102.4	1.054	67.1	0.946	57.3	0.730	37.5
Corn stover + urea	10.0	0.849	46.6	0.760	38.7	0.656	30.1
Cellulose	—	1.226	84.3	1.170	79.7	1.095	74.0
Cellulose + urea	10.0	0.981	59.8	0.794	42.1	0.618	26.3

* Portion of added organic carbon remaining. The difference required for significance between these treatments means is 4.8 at the 5 per cent level and 6.4 at the 1 per cent level.

Gaseous losses of nitrogen during decomposition of materials of varying carbon-nitrogen ratios

Although the experiments reported were planned primarily to study carbon losses during humus formation, results were also obtained in some cases on the nitrogen changes. With respect to nitrogen, information was sought on (*a*) whether addition of plant materials of wide carbon-nitrogen ratios results in appreciable biological nitrogen fixation and (*b*) at what carbon-nitrogen ratio loss of gaseous forms of nitrogen becomes appreciable. To answer these questions the limed and unlimed soils, from the 4-month incubation period, that had received the various carbon sources without supplemental urea were analyzed for total nitrogen. The results are given in table 6.

No significant gains in nitrogen occurred with any of the carbon sources added in either the acid or the limed Cecil soil. These negative results were probably due in part to the absence of Azotobacter and possibly other species of nitrogen-fixing organisms commonly found in soils of near neutral or alkaline reaction. It is also possible that some nitrogen fixation may have occurred but was either not in sufficient quantity to be detected by the Kjeldahl method or was offset by losses of ammonia or free nitrogen gas.

TABLE 6

Nitrogen losses after 4 months from Cecil soil receiving various sources of organic matter without supplemental nitrogen

All results are based on 100 gm. of soil

TREATMENT	C/N RATIO OF ADDED MATERIALS	NITROGEN ADDED IN CARBON SOURCES	UNLIMED			LIMED		
			Nitrogen found*	Nitrogen lost	Added N lost	Nitrogen found*	Nitrogen lost	Added N lost
		mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*
Soil only			37.5			35.6		
Casein	3.1	326.2	146.6	217.1	66.6	134.8	227.0	69.6
Bluegrass	9.7	103.6	124.7	16.4	15.8	108.6	30.6	29.5
Oats	10.6	94.8	111.1	21.2	22.4	100.8	29.6	31.2
Millet, young	10.7	93.2	111.7	19.0	20.4	104.1	24.7	26.5
Soybeans	15.0	66.5	96.3	7.7	11.6	85.5	16.6	25.0
Lespedeza	18.1	55.4	89.8	3.1	5.6	87.5	3.5	6.3
Millet, intermediate	34.1	29.4	64.8	2.1	7.1	64.7	0.3	1.0
Oak leaves	64.3	15.6	51.7	1.4	9.0	51.7	+0.5	+3.2
Wheat straw	73.0	13.8	49.7	1.6	11.6	47.5	1.9	17.4
Corn stover	102.4	9.8	47.1	0.2	2.0	46.0	+0.6	+6.1
Cellulose	—	0	37.0	0.5	—	36.8	+1.2	—

* Least significant difference between treatment means = 4.4 at the 5 per cent level and 5.9 at 1 per cent level.

Table 6 shows no significant loss of gaseous forms of nitrogen from the decomposing plant materials where the carbon-nitrogen ratio was 18 or wider. As the ratio narrowed from 15 to 3 the losses became increasingly larger. Bluegrass, oats, and millet, with carbon-nitrogen ratios near 10, lost about 29 per cent of their nitrogen in the limed soil and 20 per cent in the acid soil. About two thirds of the casein nitrogen was volatilized. These gaseous losses presumably occurred mostly as ammonia, although there is a possibility of some loss as free nitrogen following oxidation to nitrates. In view of the fact that plant materials having carbon-nitrogen ratios of about 28 to 35 have just enough nitrogen to permit normal decay during the first few months, gaseous losses would not be expected unless the ratio were considerably narrower than this. Just how narrow it would have to be for losses to occur would depend upon a number of factors, especially the quantity that accumulated as nitrate and the quantity held as ammonia in the exchange complex. In fact, under practical conditions, where rates of addition of plant materials to soil are usually considerably lower than those used here, losses of ammonia may be negligible because of absorption by soil colloids.

DISCUSSION

In studies in a sandy soil Engel (4) found that of the carbon added as beet leaves, lupine tops, and lupine roots 29, 19, and 36 per cent, respectively, remained after 4 months. Since all of these materials had carbon-nitrogen ratios between 11 and 15, composition was the main factor determining carbon retention.

Extensive organic matter studies were made by Salter (10) in a silt loam to which several sources of carbon and varying quantities of ammonium nitrate were added. Regardless of the source of carbon, the quantity present at the end of a year fell within a rather narrow range when the materials were adjusted to a common carbon-nitrogen ratio. Salter concluded that a ratio wider than 10 favors the loss of organic carbon from soil, whereas a narrower ratio leads to the saving of carbon. These findings are at variance with those obtained by others, including the work discussed in this and the preceding paper of the series. In evaluating Salter's results the following facts or suggestions should be considered: (*a*) The soil used contained, or formed, so much available nitrogen that even where the most carbonaceous materials were added without supplemental nitrogen, 30 to 60 pounds of nitrate nitrogen per acre was present after 1 month, and 80 to 240 pounds after 6 months. (*b*) Since all materials decomposed under conditions of adequate nitrogen, it seems probable that the higher rates of ammonium nitrate, which ranged up to 5.7 tons per acre, may have caused considerable retardation of biological activities.

Millar, Smith, and Brown (5) concluded from plant decomposition experiments that materials high in nitrogen left more carbon in the soil than did those low in nitrogen. After 190 days the carbon retention values for seven materials, having carbon-nitrogen ratios of 32 to 77, averaged 20; five other materials with ratios less than 23, averaged 32. Since the rate of release of nitrogen from the soil organic matter was high, supplemental additions would probably not have increased carbon retention; plant composition was obviously the important factor.

In greenhouse experiments, Turk and Millar (14) observed greater losses of carbon where materials of low nitrogen content were added than where more nitrogenous materials were used. At the end of the experiment 25 per cent of the carbon of straw and 34 per cent of that of sweet clover remained. Although the value of nitrogen in holding carbon is emphasized, it would seem that the experiments serve more to demonstrate the importance of plant composition. A treatment consisting of straw plus nitrogen to make the carbon-nitrogen ratio comparable to that of sweet clover was not included.

In experiments conducted in cylinders in the open, Siegel (11) added various organic materials and supplemental nitrogen in some instances, grew a crop, and determined the percentage of added carbon (exclusive of plant roots) remaining after 1 and 3 years. These results, given in part in table 7, show that the carbon of green manures was usually retained at least as tenaciously as that of straw and that addition of large amounts of nitrogen to straw had little or no effect on the quantity of added carbon that was held.

In a recent paper, Peevy and Norman (6) reported that the composition of plant materials, especially the content of lignin, materially influences the quantity and properties of the decomposed residues. Dextrose and cellulose disappeared more quickly than any other materials studied, even though adequate supplemental nitrogen was added. Furthermore, nitrogen had a negligible effect in holding the carbon of soybean stalks having a carbon-nitrogen ratio of 62.

The results reported in tables 2 to 5 are in close agreement with most of the experiments mentioned, as well as with other work (3, 13, 15), in showing that carbon retention in a normal soil is determined primarily by the chemical nature of the plant materials added. Even a unit of carbon in the form of a succulent green crop may form just as much humus as a similar amount of carbon added as a mature plant residue. This was shown very clearly in greenhouse experiments (8, 9) conducted at this laboratory. Also, in the present experiments plant composition was more important than age. There was little difference, for instance, between the behavior of succulent soybeans and lespedeza, on the one hand, and of mature wheat straw and corn stalks supplemented with urea, on the other. Other more succulent materials were somewhat less tenaciously held, but doubtless this was due more to lower lignin content than to age.

TABLE 7

Percentage of added carbon retained by a soil-sand mixture at different nitrogen levels

MATERIAL ADDED*	CARBON-NITROGEN RATIO	PERCENTAGE OF ADDED CARBON RETAINED AFTER	
		1 year	3 years
Straw	166.8	30.7	11.9
Straw	20.0	31.3	10.1
Straw	10.0	25.7	12.0
Clover	14.9	36.9	16.0
Plant mixture	13.5	32.1	17.0
Mustard	16.2	28.1	13.1
Mustard	10.0	23.9	10.6

* Materials equivalent to 0.7 per cent C were added.

The belief that nitrogen is required to hold carbon in a soil, a view held by some but certainly not all workers, is also shown to be largely without foundation, although the reverse of this statement is true, as shown in table 6. Addition of available nitrogen to nitrogen-deficient materials commonly greatly accelerates the humification process and loss of carbon during the first few weeks. There is little to indicate, however, that in absence of adequate nitrogen, the decay process, which continues slowly, leads to an excessive loss of carbon. As humus formation proceeds, most of the readily available energy sources are destroyed, whereas lignin degradation products, hemicellulose, and protein tend to accumulate either as residual materials or as products of microbial synthesis. Unless the supply of nitrogen is extremely deficient, its absence will have little effect on the nature of these transformations, although, as already stated, the rate of change will be retarded. Such extremely nitrogen-deficient conditions ordinarily occur only in an artificial medium. In a normal soil, the usual oxidation of soil organic matter with the consequent release of available nitrogen will at least eventually furnish enough supplemental nitrogen (if any is needed) for approximately maximum humus formation. Supplemental nitrogen may be, and usually is, needed to meet the needs of the crop but not to hold carbon. It should also be remembered that nitrogen additions to cropped soils commonly increase (9) soil carbon by increasing crop growth and crop residues, but there is no sound evidence that such additions exert a holding action on carbon already present in the soil or added as outside sources.

SUMMARY

Laboratory experiments are reported on humus formation, in both limed and unlimed Cecil clay loam, from plant materials of varying degrees of maturity and nitrogen content allowed to decompose for a year.

The percentages of the added carbon left in the soil after an extended period of decomposition is determined primarily by the composition of the materials added and not by their carbon-nitrogen ratios.

Contrary to popular belief, the carbon of succulent green manure crops was retained by the soil to almost as great a degree as was that of mature plant materials.

The findings do not substantiate the claim that supplemental additions of nitrogen to nitrogen-deficient crop residues are necessary to hold carbon during the process of humus formation in soil. The main effect of nitrogen additions under such conditions is to accelerate the process of humus formation and to feed the crop, if present. Where nitrogen is deficient, carbonaceous materials tend to remain in a partly decomposed condition.

It is pointed out that nitrogen additions to a cropped soil often result in a higher level of organic matter because of the resulting larger crop residues, but this effect of nitrogen falls outside the range of the present studies.

Where materials having carbon-nitrogen ratios of 18 to 102 were added to soil, no significant loss of gaseous forms of nitrogen occurred; where the ratios were 3 to 15, marked nitrogen losses occurred that increased as the nitrogen content increased. This emphasizes the importance of carbon in holding nitrogen.

Addition of calcium carbonate to an acid Cecil soil usually increased somewhat the rate of decomposition of the added carbon sources and decreased the quantity of carbon retained by the soil at the end of a year.

No significant nitrogen fixation occurred in either the limed or the unlimed

soil as a result of addition of plant materials. This may have been due to lack of Azotobacter in the original acid Cecil soil.

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PROPERTIES OF SOIL WHICH INFLUENCE WIND EROSION: II. DRY AGGREGATE STRUCTURE AS AN INDEX OF ERODIBILITY[1]

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A simple method of estimating the relative erodibility of soils by wind is of considerable practical value to agriculturists in dry-land areas. The size and stability of soil aggregates at the surface of the ground is one of the main factors that influence the erodibility of the soil by wind. Since this factor can be altered by various tillage and cropping methods, and by other means, it is important to know what type of soil structure is necessary to reduce the erodibility by wind to the practical minimum. There is likewise a need for some simple method for estimating the relative susceptibility of a soil to wind action, particularly for estimating the value of various tillage implements and cropping practices that have possibilities of use for wind erosion control.

Experiments conducted previously in a wind tunnel[2] showed an intricate relationship between the dry clod structure and erodibility by wind. Because of a relatively large number of size-fractions into which the soils were divided for detailed study, the mathematical expressions for estimating erodibility were extremely complicated. An attempt was made to incorporate the several derived expressions into a simplified general form applicable to the average range of erosive wind velocity.[3] Experimental tests proved that the general form was valid within specific limits on a large variety of soils of western Canada, but the computations were too elaborate for practical use.[4]

To achieve a simpler solution for the expression of erodibility based on the dry aggregate structure of a soil, a series of experiments were undertaken. The results of these tests and a simple method of estimating the erodibility of different soils are presented herein. Two aspects of the problem not investigated previously are included in this study: first, the possible effect of the apparent specific gravity of different soil fractions on erodibility; second, the possible degree of breakdown of soil structure during the sieving process.

PROCEDURE

The soils selected for study were all reasonably free from undecomposed crop residues, such as stubble or straw. To avoid undue breakdown of structure, the soils to be tested for erodibility were taken from the field only when in a reasonably dry condition. A square-cornered spade was pushed under a layer of surface soil 1 inch thick, and the soil was placed in a suitable tray and brought to the laboratory for thorough air-drying.

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[1] Contribution No. 414 from the department of agronomy, Kansas Agricultural Experiment Station, Manhattan, Kansas, and the Soil Conservation Service, U. S. Department of Agriculture. Cooperative research in the mechanics of wind erosion.

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After drying, the soils were placed in air-tight containers for subsequent use. Portions of some soils were passed through a specially designed rotary sieve,[5] and the various soil fractions were stored in air-tight containers to be used as required. The different fractions into which the soils were sieved were as follows: A, <0.42 mm. in diameter; B, 0.42 to 0.84 mm.; C, 0.84 to 6.4 mm.; D, >6.4 mm.

To test the erodibility of the various soils, or mixtures of the various soil fractions, use was made of a closed-circuit type wind tunnel described previously.[6] The soils were subjected to a wind equivalent to 25 miles per hour under standard temperature and pressure at a 6-inch height. The soil samples were placed in a trough 5 feet long, 8 inches wide, with open ends. The soil surface was leveled by hand. Some differences in the degree of surface roughness existed on the different soils, but these were due to differences in the size of the fractions and not to differences in the treatment. The trough with the soil was placed on the leeward end of the test chamber parallel to the direction of the wind and level with the remaining floor area. The remaining floor area of the test chamber was covered with gravel 2.0 to 6.4 mm. in diameter.

Erosion continued for a relatively short time on all soils tested and ceased as soon as the surface became stabilized with fractions too large to be moved by wind. The quantity of soil eroded up to the time when movement ceased constituted a measure of erodibility. The time required for movement to cease varied considerably with soil structure—the range being approximately 10 to 60 minutes.

The apparent specific gravity or volume weight of the soil grains of each size-fraction separated by sieving was determined by dividing the weight of a definite volume of the fraction by the weight of an equal volume of quartz sand containing the same sized grains as the soil fraction and multiplying the quotient by 2.65. The quartz grains used were uniform in composition, entirely devoid of pore spaces, and had a specific gravity of 2.65. The apparent specific gravity thus determined represented the volume weight of the individual soil grains or aggregates and not the volume weight of the soil body or bed composed of these grains. The apparent specific gravity of soil clods greater than 6.4 mm. in diameter was determined by the usual liquid displacement method after the clods were coated with a thin, impermeable film of paraffin wax.

RESULTS

Erodibility of mixtures of different soil aggregates

Figure 1 indicates the quantities of soil removed by wind when the highly erodible fraction A, separated from three widely different soil classes by sieving, is mixed with different amounts of similar textured, nonerodible fractions C and D. When the amount of fractions C and D is plotted against the logarithm of the amount eroded, the resultant curves are nearly straight. Evidently, each increment of the nonerodible fraction C or D added to the synthetic mixture with fraction A reduces the logarithm of the amount eroded almost equally. With very low concentrations of C or D, the logarithm of the amount eroded deviates slightly upward from the linear relationship, and with very high con-

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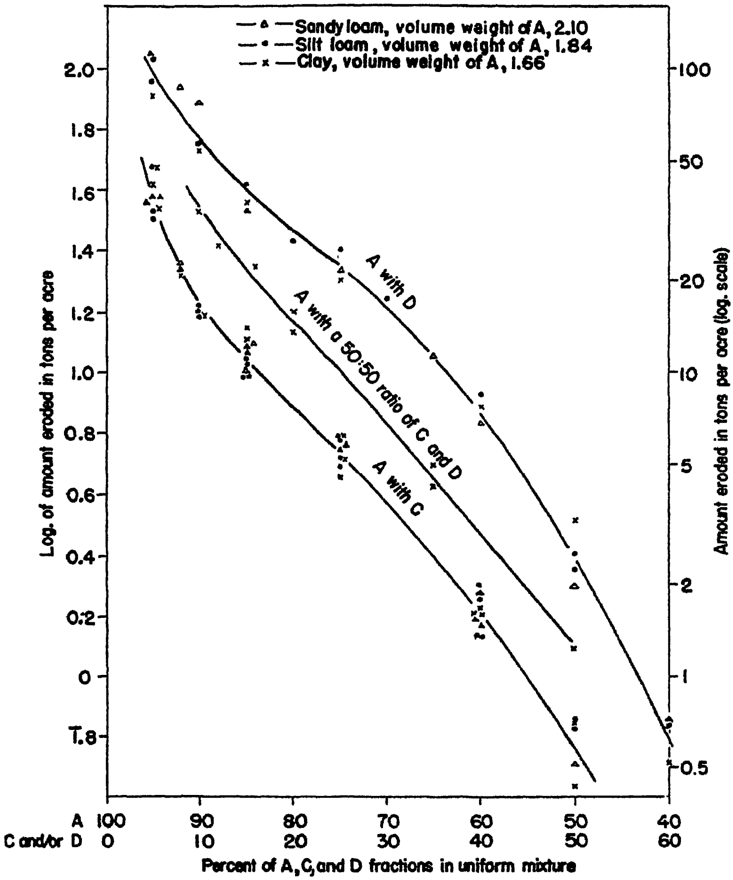

FIG. 1. EFFECT OF FRACTIONS C AND D ON ERODIBILITY OF FRACTION A

centrations, slightly downward. The plotted curves thus assume a slight "S" curvature.

The experimental data in figure 1 show the erodibility of any mixture of A with C, A with D, and A with C and D. An equal proportion of C and D mixed with A gives the logarithmic values of erodibility half way between the values where only C or D alone is mixed with A. These data, and especially those of figure 2, show that the logarithm of the amount eroded varies directly and proportionately with the ratio of C to D contained in the soil. Thus, if the soil is composed of 20 per cent of C mixed with A, the logarithm of the amount eroded in tons per acre is shown to be 0.9; and if it is composed of 20 per cent of D mixed with A the logarithm of the amount of erosion is 1.5. On the other hand,. if it contains a mixture of C and D amounting to 20 per cent of the total, the logarithm of the amount eroded varies directly with the relative proportion of C and D and is equal to

$$\frac{0.9\,\mathrm{C} + 1.5\,\mathrm{D}}{\mathrm{C} + \mathrm{D}},$$

where C and D are the percentages of fraction C and D. The actual erodibility of the whole range of uniform mixtures of fractions A, C, and D applicable to the conditions of the wind and the soil under which the tests were conducted can thus be determined by interpolation or direct reading of experimental values in figures 1 and 2. These values are presented in rather broad increments in table 1. Erosion values less than 0.1 ton per acre are considered too small to be of any significance and are, therefore, omitted from table 1.

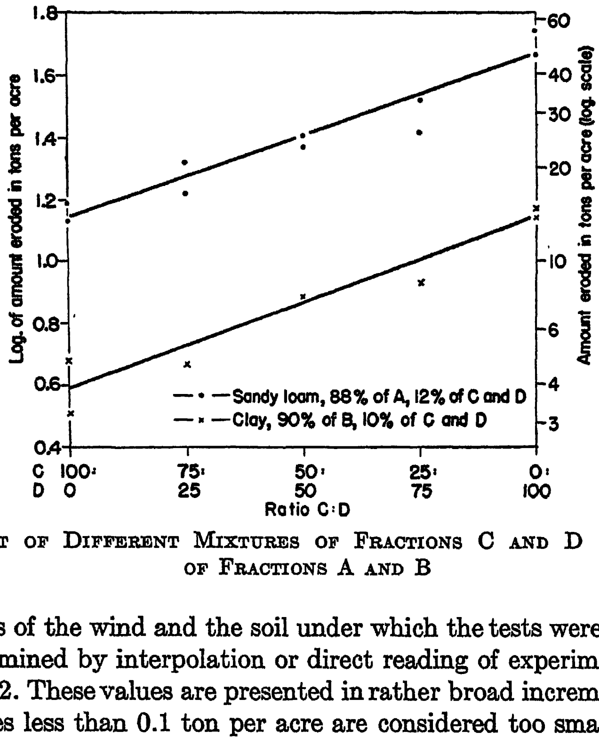

FIG. 2. EFFECT OF DIFFERENT MIXTURES OF FRACTIONS C AND D ON ERODIBILITY OF FRACTIONS A AND B

Some consideration was given to the possible effect of apparent specific gravity of the different fractions on erodibility. In the soils used, the range of apparent specific gravity of fractions C and D, which was between 1.46 and 1.66, was too narrow to determine what effect it might have on erodibility.

The apparent specific gravity of fraction A varied considerably more, that is, from 1.66 to 2.10. Figure 1 shows that this range of variation for fraction A has little, if any, effect on erodibility. Further studies are undertaken to obtain information on the possible effects of a wider range of apparent specific gravity of the various soil fractions on erodibility.

TABLE 1

Erodibility x *in tons per acre for any proportion of fractions C and D in mixture with A**

PER CENT FRACTION D	PER CENT FRACTION C																					
	0	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	24	28	32	36	40	44
0	∞	—	—	69.0	48.0	38.4	30.9	25.7	22.1	19.5	17.4	14.4	12.1	10.2	8.9	7.8	5.8	4.4	3.2	2.3	1.5	1.1
1	—	—	77.5	61.3	46.1	37.8	30.5	25.7	22.1	19.5	17.4	14.3	12.0	10.1	8.8	7.7	5.7	4.2	3.0	2.1	1.4	1.0
2	—	82.0	69.0	57.5	44.3	36.5	30.0	25.5	22.0	19.4	17.4	14.3	11.9	10.0	8.6	7.6	5.5	4.0	2.7	2.0	1.4	1.0
3	117.0	77.0	63.0	53.6	41.6	35.0	29.4	25.2	21.8	19.4	17.4	14.2	11.8	9.9	8.5	7.5	5.3	3.9	2.5	1.9	1.3	0.9
4	106.0	72.3	57.8	49.5	39.0	33.5	28.7	24.7	21.6	19.1	17.1	13.9	11.6	9.8	8.4	7.4	5.1	3.7	2.4	1.8	1.2	0.8
5	95.5	69.0	53.3	46.0	37.5	32.0	27.9	24.1	21.3	18.8	16.8	13.6	11.4	9.6	8.2	7.3	4.9	3.5	2.3	1.7	1.2	0.8
6	85.3	63.8	50.3	42.6	35.2	30.7	27.0	23.5	20.9	18.4	16.4	13.3	11.1	9.5	8.1	7.1	4.8	3.3	2.2	1.6	1.1	0.7
7	77.1	58.8	47.5	39.8	33.8	29.5	26.0	22.9	20.5	18.1	16.1	13.0	10.9	9.4	8.0	6.9	4.7	3.1	2.1	1.5	1.0	0.7
8	70.8	55.0	44.8	37.1	32.0	28.3	25.1	22.2	20.1	17.7	15.8	12.7	10.7	9.2	7.8	6.6	4.6	3.0	2.0	1.4	1.0	0.6
9	64.8	52.0	42.2	34.7	30.6	27.2	24.2	21.6	19.6	17.3	15.6	12.4	10.4	9.0	7.6	6.4	4.5	2.8	1.9	1.3	0.9	0.6
10	59.9	49.0	39.7	33.0	29.0	26.0	23.3	21.0	19.0	17.0	15.3	12.1	10.1	8.7	7.3	6.2	4.3	2.7	1.8	1.2	0.9	0.5
12	52.4	42.7	35.1	29.5	26.4	23.7	21.5	19.5	17.7	16.0	14.4	11.6	9.7	8.3	6.9	5.8	4.0	2.4	1.6	1.1	0.7	0.4
14	46.8	37.2	31.7	26.6	23.9	21.7	19.7	18.0	16.4	15.0	13.5	11.0	9.2	7.8	6.4	5.4	3.6	2.2	1.4	0.9	0.5	0.3
16	41.2	32.8	27.9	24.0	21.6	19.8	18.1	16.5	15.1	14.0	12.6	10.4	8.6	7.2	6.0	4.8	3.2	1.9	1.2	0.8	0.4	0.2
18	35.9	28.6	24.9	22.0	19.8	18.0	16.5	15.1	14.0	13.0	11.8	9.8	8.1	6.8	5.4	4.2	2.8	1.7	1.1	0.7	0.4	0.1
20	30.7	25.3	22.4	20.1	18.2	16.5	15.1	13.8	12.9	12.0	11.0	9.2	7.7	6.4	5.0	3.6	2.4	1.5	1.0	0.6	0.3	
22	25.7	22.3	20.1	18.2	16.4	14.9	13.6	12.6	11.7	10.9	10.1	8.5	7.1	5.9	4.5	3.2	2.2	1.3	0.9	0.5	0.2	
24	22.1	19.9	18.0	16.2	14.7	13.3	12.2	11.3	10.5	9.9	8.9	7.7	6.5	5.4	4.1	3.0	2.0	1.1	0.7	0.3	0.1	
26	19.7	17.7	16.0	14.3	13.1	11.9	11.0	10.2	9.5	8.8	8.1	6.9	5.9	4.8	3.7	2.8	1.7	1.0	0.6	0.2		
28	17.7	15.9	14.2	12.8	11.6	10.7	9.9	9.2	8.5	7.9	7.2	6.1	5.3	4.2	3.3	2.6	1.5	0.8	0.4	0.1		
30	15.8	14.1	12.7	11.4	10.5	9.6	8.8	8.2	7.6	7.0	6.4	5.4	4.6	3.8	2.9	2.3	1.3	0.6	0.2			
34	12.2	10.7	9.5	8.5	7.7	7.0	6.4	5.8	5.3	4.9	4.6	3.9	3.1	2.5	1.9	1.5	0.8	0.3	0.1			
38	8.8	7.4	6.4	5.7	5.1	4.5	4.1	3.7	3.4	3.1	2.9	2.5	2.1	1.7	1.3	1.0	0.4	0.1				
42	6.0	5.0	4.2	3.8	3.3	2.9	2.6	2.4	2.2	2.1	1.9	1.6	1.3	1.1	0.9	0.6	0.2					
46	3.9	3.3	2.8	2.6	2.2	2.0	1.8	1.6	1.4	1.3	1.2	1.0	0.8	0.7	0.5	0.2						
50	2.5	2.1	1.8	1.6	1.4	1.3	1.2	1.1	1.0	0.9	0.8	0.6	0.4	0.2	0.1	0.1						
54	1.6	1.3	1.2	1.1	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1								
58	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.2	0.1	0.1										
62	0.6	0.5	0.4	0.3	0.2	0.1	0.1	0.1														

* Erodibility for a 5-foot length of exposed area; a wind blowing from one direction at 25 m.p.h. at a 6-inch height; an apparent specific gravity of 1.5 to 1.7 for fractions C and D and 1.6 to 2.1 for fraction A.

The effect of the semierodible fraction B remains to be clarified. Figures 3, 4, and 5 show the results obtained when this fraction is mixed with the nonerodible fractions. The curves correspond in slope and shape approximately to those in which A instead of B is the erodible fraction. Only the position of the curves is altered. Figures 3 and 4 show that when A of any apparent specific gravity and mixed with any quantity of C or D is replaced by B of 1.6 apparent specific gravity the logarithm of the amount eroded is decreased by approximately 0.55.

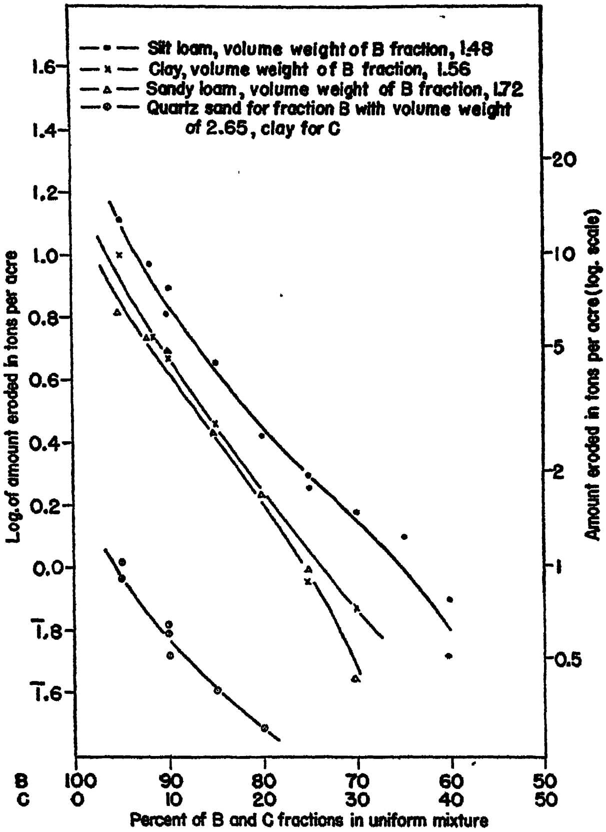

FIG. 3. EFFECT OF FRACTION C ON ERODIBILITY OF FRACTION B

In other words, the replacement of A by B of 1.6 apparent specific gravity reduces the amount of erosion x to $\frac{x}{3.55}$. Figure 5 indicates further that if only a part of fraction A is replaced by B, the logarithm of the amount eroded is decreased in proportion to the part displaced. Thus, let it be assumed that the amount of erosion for any mixture of A, C, and D, such as shown in table 1, is x, then the amount of erosion when A is replaced by B of 1.6 apparent specific gravity is antilog ($\log x - 0.55$). If only part of A is replaced by B, the amount of erosion is antilog

$$\left(\log x - 0.55 \frac{\%\text{B}}{\%\text{A} + \%\text{B}}\right)$$

The apparent specific gravity of fraction B, contrary to that of A, has a considerable influence on the amount of erosion. As shown in figures 3 and 4, the logarithm of the amount eroded is inversely proportional to the apparent specific gravity of B, irrespective of whether B is mixed with C or D. It will be seen that for every 0.1 decrease in the apparent specific gravity of B, mixed with C or D, there is approximately a 0.1 decrease in the logarithm of the amount eroded.

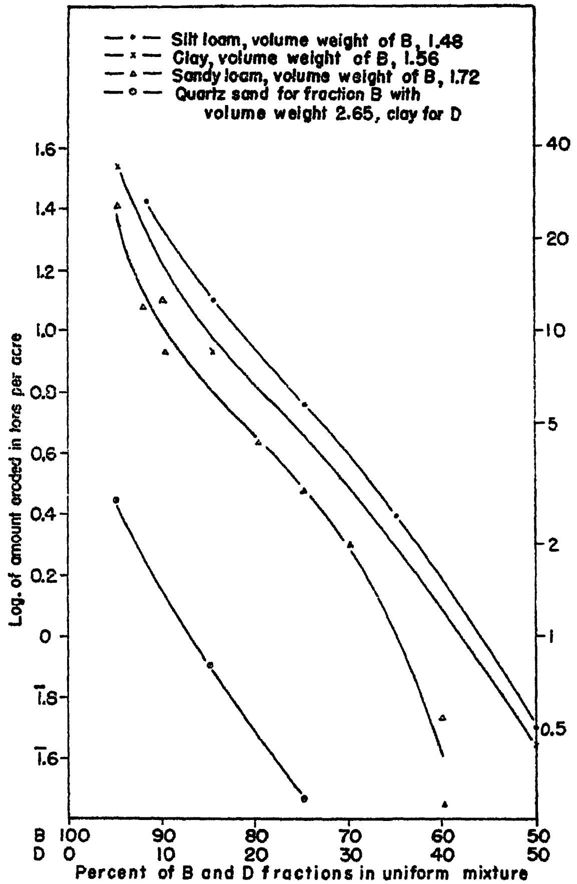

FIG. 4. EFFECT OF FRACTION D ON ERODIBILITY OF FRACTION B

The effect of the total or partial replacement of A by B and the effect of the apparent specific gravity of B on erodibility may be indicated from the data available by the expression:

$$q = \text{antilog}\left[\log x - (0.55 + \sigma_{\text{B}} - 1.6)\frac{\%\text{B}}{\%\text{A} + \%\text{B}}\right]$$

or

$$q = \frac{}{\text{antilog}\left[(0.55 + \sigma_{B} - 1.6)\,\dfrac{\%B}{\%A + \%B}\right]}$$

where q is the ultimate amount of erosion, x is the amount of erosion for a soil in which the erodible fractions are composed entirely of fraction A, and σ_{B} is the apparent specific gravity of fraction B.

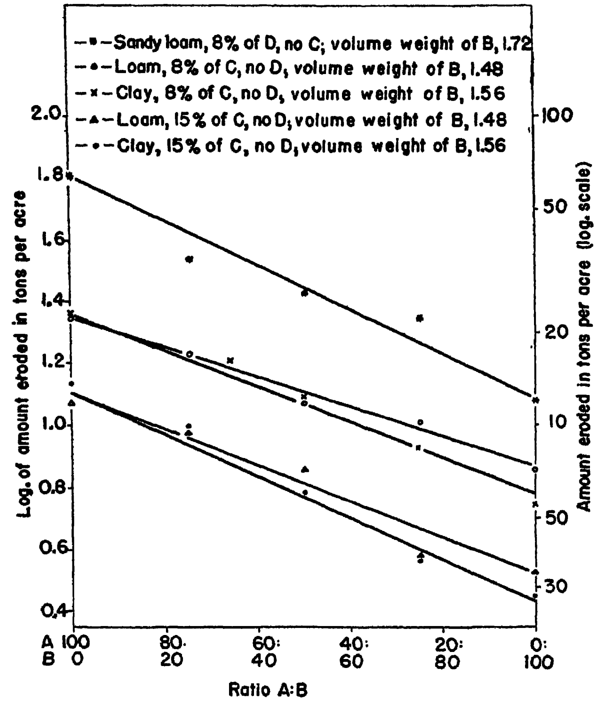

FIG. 5. EFFECT OF FRACTIONS C AND D ON ERODIBILITY OF DIFFERENT MIXTURES OF A AND B

The values of the divisor, antilog

$$(0.55 + \sigma_{B} - 1.6)\,\frac{\%B}{\%A + \%B},$$

for the whole working range of apparent specific gravity of B and of proportion of B to A are prepared in table 2 by interpolation of the experimental data obtained. By determining the proportions of soil fractions A, B, C, and D by sieving, the erodibility of any soil reasonably free from stubble, straw, or other types of organic residue, may thus be readily determined from tables 1 and 2. To avoid superfluity, the values of erodibility are presented in rather broad increments in tables 1 and 2. More detailed tables were prepared, however, for greater convenience in practical use.

Comparison of computed with determined order of erodibility

To check the validity of tables 1 and 2 for estimating the erodibility of different soils by the sieving method, a series of wind tunnel tests were conducted.

TABLE 2

Divisors for erosional values in table 1, as influenced by proportion and apparent specific gravity of fraction B contained in the soil

RATIO $\frac{\% B}{\% A + \% B}$	APPARENT SPECIFIC GRAVITY OF FRACTION B								
	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
.02	1.00	1.01	1.02	1.03	1.04	1.05	1.05	1.06	1.07
.04	0.99	1.01	1.03	1.05	1.07	1.09	1.10	1.13	1.15
.06	0.99	1.02	1.05	1.08	1.10	1.14	1.17	1.21	1.23
.08	0.99	1.03	1.07	1.11	1.15	1.19	1.23	1.27	1.32
.10	0.99	1.04	1.09	1.13	1.19	1.25	1.30	1.37	1.43
.12	0.99	1.04	1.10	1.17	1.23	1.30	1.37	1.45	1.53
.14	0.98	1.05	1.12	1.20	1.27	1.36	1.45	1.55	1.64
.16	0.98	1.06	1.14	1.23	1.32	1.42	1.53	1.65	1.77
.18	0.98	1.07	1.16	1.26	1.37	1.48	1.61	1.75	1.90
.20	0.98	1.07	1.18	1.29	1.42	1.55	1.70	1.86	2.03
.22	0.98	1.08	1.20	1.32	1.47	1.62	1.79	1.98	2.18
.24	0.97	1.09	1.21	1.36	1.51	1.69	1.89	2.11	2.35
.26	0.97	1.09	1.23	1.39	1.57	1.77	1.99	2.24	2.53
.28	0.97	1.10	1.25	1.42	1.62	1.85	2.10	2.39	2.71
.30	0.97	1.11	1.27	1.46	1.68	1.93	2.22	2.54	2.91
.32	0.96	1.12	1.29	1.50	1.74	2.02	2.34	2.71	3.14
.34	0.96	1.13	1.32	1.54	1.80	2.10	2.46	2.88	3.38
.36	0.96	1.13	1.34	1.58	1.86	2.20	2.59	3.06	3.61
.38	0.96	1.14	1.36	1.62	1.93	2.30	2.74	3.26	3.87
.40	0.96	1.15	1.38	1.66	2.00	2.40	2.88	3.46	4.15
.42	0.95	1.16	1.40	1.70	2.06	2.50	3.04	3.70	4.48
.44	0.95	1.16	1.43	1.74	2.14	2.62	3.20	3.93	4.81
.46	0.95	1.17	1.45	1.79	2.22	2.74	3.38	4.18	5.17
.48	0.95	1.18	1.48	1.83	2.30	2.86	3.56	4.45	5.55
.50	0.94	1.19	1.50	1.88	2.38	2.98	3.76	4.73	5.96
.52	0.94	1.20	1.52	1.93	2.46	3.12	3.96	5.04	6.40
.54	0.94	1.20	1.54	1.98	2.54	3.26	4.18	5.36	6.88
.56	0.94	1.21	1.57	2.03	2.63	3.40	4.41	5.70	7.38
.58	0.94	1.22	1.59	2.08	2.72	3.56	4.65	6.06	7.93
.60	0.93	1.23	1.62	2.14	2.82	3.71	4.90	6.45	8.52

The erodibility of 15 widely different soils and composites of these soils from central and western Kansas was determined directly in the wind tunnel (table 3). Portions of the same soils not exposed to the wind in the tunnel were passed through a rotary sieve to determine the relative proportions of fractions A, B, C and D. The erodibility of each soil was then computed from values in tables 1 and 2.

A comparison of the eroded with the computed amounts can be made from table 3, columns 8 and 10. In virtually all cases the computed values were somewhat higher than the eroded values. To determine whether sieving was responsible for the increase in erodibility, the fractions obtained from the same soil by sieving were thoroughly but gently mixed, and the mixtures were exposed to the same velocity of wind in the tunnel. The actual amounts of erosion on samples of soil that had been previously sieved were, in most cases, somewhat higher than on soils not previously sieved, but were, on the whole, the same as the computed values. Since the computed values were also based on sieved soil materials, the results prove that sieving had a considerable effect in increasing the erodibility. The increase in erodibility is presumed to be caused by the breakdown of the soil aggregates during the sieving process. The average increase in erodibility due to sieving was 11.8 per cent.

TABLE 3

*Comparison of determined with calculated erodibility of various types of cultivated soil**

SOIL TYPE OR CLASS	SOIL NO.	SIZE DISTRIBUTION OF FRACTIONS				VOLUME WEIGHT OF FRACTION B	AMOUNT ERODED IN TUNNEL BEFORE SIEVING	AMOUNT ERODED IN TUNNEL AFTER SIEVING	AMOUNT COMPUTED
		A	B	C	D				
		per cent	*per cent*	*per cent*	*per cent*		*tons/A.*	*tons/A.*	*tons/A.*
Loamy sand (Syracuse, Kansas)	60	91.3	1.6	5.3	1.8	1.56	27.0	35.5	34.8
Composite of soil 42 and 60	60a	83.9	6.8	5.7	3.6	1.64	28.1	31.5	29.4
Composite of soil 42 and 60	60b	78.1	7.7	4.0	10.2	1.82	23.1	22.8	24.8
Composite of soil 42 and 60	60c	77.4	6.9	4.9	10.8	2.00	21.8	19.4	20.8
Composite of soil 42 and 60	42a	74.4	7.4	5.9	12.3	2.18	11.7	9.8	16.7
Pratt loamy sand	42	74.0	7.6	8.2	10.2	2.19	13.9	18.2	15.0
Dalhart fine sandy loam	55	68.9	11.1	11.8	8.2	1.80	8.0	11.7	10.0
Pratt loamy sand	39	63.9	15.4	10.1	10.6	2.00	6.1	6.2	9.7
Silt loam (Winona, Kansas)	62	60.0	9.8	17.6	12.6	1.37	4.5	5.7	6.1
Silty clay loam (Collyer, Kansas)	63	52.2	15.9	10.5	21.4	1.61	4.4	5.0	7.4
Silt loam (Tribune, Kansas)	61	57.6	12.8	18.5	11.1	1.49	4.5	5.1	5.6
Silt loam (Johnson, Kansas)	59	57.2	12.0	20.6	10.2	1.47	4.2	4.8	4.8
Baca silt loam	57	51.8	14.6	13.2	20.4	1.76	3.2	3.3	5.8
Alluvial clay (Salina, Kansas)	52	38.9	26.0	15.7	19.4	1.69	2.9	3.3	3.6
Loamy sand (Hugoton, Kansas)	54	41.9	21.5	20.5	16.1	2.06	1.7	2.0	2.0
Soil 33 with fine fractions added	33c	41.4	9.4	21.7	27.5	1.61	0.8	0.7	1.5
Soil 33 with fine fractions added	33b	35.6	13.4	26.5	24.5	1.60	0.3	0.6	0.9
Soil 33 with fine fractions added	33a	27.7	13.5	28.3	30.5	1.51	0.3	0.6	0.4
Richfield silt loam	33	24.2	9.5	22.7	43.6	1.46	0.2	0.3	0.2
Larned sandy loam	36	25.1	7.2	20.7	47.0	1.67	0.3	0.3	0.1
Hastings silt loam	30	16.9	10.5	36.9	35.7	1.55	0.2	0.2	<0.1
Ulysses silt loam	16	15.1	8.7	27.9	48.3	1.62	0.2	0.2	<0.1

* All soils were virtually devoid of crop residues, such as stubble or straw.

The computed amounts of erosion were plotted against the amounts eroded in the tunnel after soil sieving. The data indicated that the computed amounts varied directly and almost proportionately with the actual amounts of erosion. The coefficient of correlation between the computed amounts of erosion and amounts eroded before and after soil-sieving was 0.98 in both cases. For 20 degrees of freedom this is far above the 1 per cent level of significance, which is 0.54. The data indicate that tables 1 and 2 can be employed with a reasonable degree of accuracy as a simple method of measuring the erodibility of cultivated soils by wind. The ease of measurement can be enhanced by incorporating into tables 1 and 2 erodibility values for increments considerably smaller than the given ones. The accuracy of the measurements could be increased further by increasing the number of sievings in each test. These measurements are determined entirely from the dry aggregate soil structure. Organic residues such as stubble or straw, not present in these experiments, are expected to have an additional effect on erodibility.

To test further the validity of tables 1 and 2, a statistical analysis of data obtained previously on 30 western Canada soils was made. The apparent specific gravity of fraction B, not available for these data, was assumed to be 1.6. When the two trace values of estimated erodibility are excluded, the number of degrees of freedom for this group of soils is 26. The coefficient of correlation between erodible amounts estimated from tables 1 and 2 and the amounts eroded in a wind tunnel is 0.98. This is very highly significant, since the required value for significance at the 1 per cent level is 0.48. Tables 1 and 2, therefore, appear to be highly applicable to a wide variety of soils of western Canada as well as to soils of Kansas.

DISCUSSION AND CONCLUSIONS

Soil erodibility as determined by computation based on the dry-sieving procedure is a measure of the relative amount of soil erodible from a definitely restricted area by a definite velocity of wind blowing from one direction. Because the size of the exposed soil area on which the measure of erodibility is based is restricted to a few square feet in the tunnel, the effects of abrasion such as occur in comparatively large areas in the field are virtually eliminated. The amounts of soil erodible in the wind tunnel may be expected, therefore, to be lower than the amounts in the open field. Nevertheless, the basis which determines the relative degree of erosion from field areas and from small samples placed in the tunnel appears to be the same. This basis is the quantity of erodible fractions removable from the surface of the soil by wind.

The comparative amounts of erosion computed from the dry aggregate structure of a soil are about 12 per cent higher than the actual amounts eroded in the tunnel. It is not known what ratio the computed amounts of erosion bear to the amounts erodible in the open field. This ratio will vary, of course, unless the fields chosen for comparison are all of the same dimensions and the same orientation with respect to the direction of the wind.

The computed erosion values cannot be expected to serve as a measure of the inherent erodibility but rather as a measure of the relative erodibility at the time the determinations are made. The dry aggregate structure, as well as the erodibility, varies from season to season and virtually from day to day, depending on weather conditions and on tillage and cropping practices.

The apparent specific gravity of the different soil fractions affects the erodibility in a variable degree. The major effects of the apparent specific gravity have been determined in this investigation and incorporated into the computation method. More details are necessary, however, for a thorough understanding of the relationship of this factor to erodibility by wind.

The computed erosion values are expected to apply particularly to soils that have been recently cultivated, such as the ones on which these experiments were based. A previous study showed, however, that the computed erodibility based on the dry aggregate structure of soils is a reliable index of the actual erodibility of less recently cultivated soils as well as of freshly cultivated soils.

In determining the relative erodibility from the dry aggregate soil structure, care must be taken to avoid undue breakdown of soil aggregates and undue segregation of the finer fractions from the coarser ones. Since dry-sieving is responsible for some breakdown of the soil aggregates, it is important that a uniform sieving technique be followed in all comparable cases. The rotary sieve was found most suitable for this purpose.

SUMMARY

A simple method of computing the erodibility of cultivated soils by wind is presented. The computed erosion values are based on soils with a smooth surface free from organic residues. After determination of the apparent specific gravity and of the proportions of dry soil fractions by sieving, the relative erodibility of any soil reasonably free from organic residues can be readily computed from the tables presented. Similar but more detailed tables, not presented, have been prepared for greater ease and accuracy of computing the erodibility.

BOOKS

Adaptation and Origin in the Plant World. By Frederick E. Clements, Emmett V. Martin, and Francis L. Long. The Chronica Botanica Company, Waltham, Mass., and Stechert-Hafner, Inc., New York, 1950. Pp. 332, plates 85, figs. 7, graphs, 21. Price $6.

This is a monograph on the role of environment in the evolution of plants. It deals primarily with studies carried on for 40 years in a coastal laboratory and two control experimental gardens near Santa Barbara, California, and in an alpine laboratory and three transplant gardens near Colorado Springs. The several chapters have to do with the installation of the gardens near Santa Barbara, and the function, form, and behavior of the plants, and the installation of the Colorado Springs gardens, and functions, ecogenesis, morphogeny, and phylogeny of these plants. Some 200 genera and 400 species of plants were studied. A glossary of terms is appended. The book is of primary interest to ecologists, but the methods of experimentation and some of the conclusions are of considerable importance to other workers in soil-plant science. The illustrations are especially interesting and attractive.

Biologie der Goethezeit. Edited by Adolf Meyer-Abich. The Chronica Botanica Co., Waltham, Mass., 1949. Pp. 302. Price $5.50.

The editor brings together in one volume the more important concepts of Johann Wolfgang v. Goethe and the other outstanding biologists of his time, including Georg Foster, Alexander v. Humboldt, Lorenz Oken, Carl Gustav Carus, Karl Ernest Baer, and Johannes Müller. Extracts from the publications of these men include an introduction dealing with Goethe's researches and their philosophical-historical meaning; Forster's comprehensive view of nature; Humboldt's vital energy; Oken's scientific classification of animals; Carus' requirements for future work in the natural sciences; Baer's view of the living world; Müller's philosophical approach to physiology; and a final chapter on Goethe's principle of compensation, a basic law of modern biology. A full-page photograph of each man is included. German scholars will find this book worthy of careful study.

Decay of Timber and Its Prevention. By K. St. G. Cartwright and W. P. K. Findlay. Chemical Publishing Co., Inc., Brooklyn, 1950. Pp. 294, plates 49. Price $7.50.

The authors of this book are members of the staff of the Forest Products Research Laboratory at Aylesbury, Bucks. They have brought together in this volume a series of publications on the principal decays of oak, softwoods, and British hardwoods. Different types of decay, resistance to decay, wood preservatives and their use, and staining by fungi and its prevention are considered in detail. A long list of references is appended to each chapter. Proper spacing of trees to develop a clean bole is stressed as a means of avoiding entrance of decay organisms. A list of the most durable woods is shown. The appendix describes the wood block method of test for the toxicity of preservatives to fungi. The book is of special importance to those who are concerned with forestry, but it contains material of considerable interest to all those who have trees of whatever type on their property.

Evergreen Orchards. By WILLIAM H. CHANDLER. Lea and Febiger, Philadelphia, 1950. Pp. 452, figs. 66. Price $6.

A lifetime of study and research has gone into the writing of this very interesting and attractive book. Its purpose is to serve the needs of students who are specializing in subtropical and tropical horticulture. The several chapters deal with a wide range of fruits, including citrus, avocado, papaya, tea, coffee, cacao, annonas, lichti, mango, cashew, evergreen nuts, olive, date, cocoanut, and banana. The first two chapters cover the tree and its fruit and the means of controlling the environment, with special reference to soil factors. The cover shows an orange grove in color, with a snow-capped mountain in the background. The illustrations throughout the book are excellent. The appendix contains 687 references to important literature, which are arranged by chapters. So much of the material is of such general interest as to justify having the book available in all agricultural libraries. The book represents a highly important contribution to the literature in the horticultural field.

An Exploratory Study of Soil Groups in the Belgian Congo. By CHARLES E. KELLOGG AND FIDELIA D. DAVOL. L'Institut National pour l'Étude Agronomique du Congo Belge, Brussels, 1949. Pp. 73, figs. 35. Price, paper bound, 100 fr.

This study, number 46 of a scientific series of the I.N.E.A.C., is purely exploratory, but it provides some very interesting material on the soils and agriculture of the Belgian Congo. Laboratory studies on some 25 representative soil profiles are reported. The soils are, for the most part, classified as latosols, with some red prairie and red-yellow and brown podzolic soils, and ground-water laterites. The data include pH values, phosphorus, organic matter, exchangeable cations, exchange capacity, and clay minerals. Special emphasis is placed on rotational forestry as a means of collecting mineral nutrients at the soil surface for use in crop production. This is a highly interesting and very constructive report.

Frontiers in Colloid Chemistry. Edited by R. E. BURK AND OLIVER GRUMMITT. Interscience Publishers, New York, 1950. Pp. 157. Price $4.

Frontiers in chemistry, of which this is volume 8, is a series published under the auspices of Western Reserve University. This volume contains chapters on role of adsorption in colloid science, by Hugh S. Taylor; frontiers in chromatographic adsorption analysis, by Harold H. Strain; ion exchange, with special reference to synthetic resins, by Robert J. Meyers; sedimentation, by V. R. Damerell; colloidal electrolytes, wetting agents, and detergents, and organization of crystals and micelles of soap: solubilization and detergency, by James W. McBain. A long list of references is appended to each chapter. Most of the material is of much interest and value to soil physicists and physical chemists and should be made available to all graduate students in soils.

List of Plant Breeders in Canada and the United States of America. By Food and Agricultural Organization of the United Nations. Columbia University Press, New York, 1949. Pp. 64. Price $0.75.

This is a reference list of classified information giving the names and addresses of the plant breeders in Canada and the United States and the specific plants with which they are working. It is interesting to note that 60 men are breeding alfalfa, 95 barley, 51 cotton, 107 maize, 90 oats, 53 potato, and 116 wheat. Among the tree plants are maple, ash, papaw, beach plum, elm, pea, pecan, chestnut, cedar, filbert, fig, apple, peach, pine, pear, larch, poplar, and spruce. A great variety of smaller plants are listed, including bentgrass, onion, bacteria, buckwheat, buffalo grass, chicory, cranberry, crocus, fungi, lichti, lupine, rape, rubber, safflower, squill, and trefoil.

Microbiologie du Sol. By S. WINOGRADSKY. Masson et Cie, Paris, 1949. Pp. 861. Price, paper bound, 3,000 fr.

Every soil microbiologist will want a copy of this volume, containing all of the author's publications that appeared over the period of 50 years during which he was engaged in research in this field. With two exceptions, in English, all the papers are in French. The material is of great interest to those who desire to know something about the beginnings of soil microbiology, notably that part having to do with nitrification, nitrogen fixation, and the iron and sulfur bacteria. The several chapters deal with autotrophes, morphology of bacteria, nitrification, anaerobic fixation, retting of flax, microbiological ecology. Winogradsky began his studies in 1885, and his first paper, on sulfur bacteria, was published in 1887. For a part of the 63-year period since that date, he was engaged in private business, but he returned to the field of microbiology in 1922 when he accepted an appointment at the Institut Pasteur. He has since been at Brie-Comte-Robert, where he is still actively engaged in study and research. The volume contains all the original illustrations and is of great historical value.

Phenomena, Atoms and Molecules. By IRVING LANGMUIR. Philosophical Library, Inc., New York, 1950. Pp. 436. Price $10.

For 40 years the author of this book has occupied a unique position in that he has enjoyed "more academic freedom" in a large industrial laboratory than he ever had encountered in a university, and he had sufficient funds at his disposal to finance whatever he saw fit to do. The book begins with a chapter on science, common sense, and decency, then considers science legislation and world control of atomic energy, and finally deals more specifically with the author's researches on surface chemistry, orientation of molecules, atomic hydrogen, forces near the surfaces of molecules, isomorphism, molecular dissymmetry, metastable atoms and electrons, gas molecules, evaporation of molecules, atoms, ions, and electrons, mobility of caesium atoms adsorbed on tungsten, and types of valence. The bibliography is a list of the author's 215 publications arranged according to subject matter. Of these papers, 20 are reprinted in full in this volume. The book is of special interest to those who are concerned with the physicochemical aspects of soil-plant science.

Plant Ecology Work Book. By J. T. Curtis. Burgess Publishing Co., Minneapolis, 1950. Pp. 39. Price $1.75.

This laboratory, field, and reference manual is designed for a one-semester course in ecology. It outlines eight laboratory exercises on morphological adaptations to the water factor, effect of soil moisture on plant growth, effect of soil type on plant growth, tree ring studies, fossil pollen analyses, measurement of environmental factors, use of sampling methods, and denudation quadrats. The reference material covers species composition of the several forest and prairie areas, and vegetation, soils, and climatic maps for Wisconsin. Some 150 references are appended. In addition there are some 75 hardwood forest data sheets for field use with spaces for filling in the ecological data. This is an attractively prepared manual, which should be very useful to instructors in this subject.

Soils of Wisconsin in Relation to Silviculture. By S. A. Wilde, F. G. Wilson, and D. P. White. Wisconsin Conservation Department, Madison, 1949. Pp. 171, figs. 74. Price, paper bound, $1.

The authors are concerned with those aspects of soils that are of special interest to foresters. Concrete examples are given of the part soil plays in the selection of species for reforestation, in tree-planting techniques, in rate of growth, in protection against parasites, and in conservation. But the book will be of considerable interest to all students of the origin and nature of soils. The material is classified under immature soils, soils in the podzol region of conifers and northern hardwoods, and soils in the prairie-forest region of oak and associated hardwoods. The illustrations are especially interesting and attractive. The appendix contains tables on the major characteristics of Wisconsin's soil-forest types, planting-site requirements of tree species commonly planted or adapted to Wisconsin, common and scientific names of Wisconsin trees and shrubs, and a glossary of important terms pertinent to soils and forests. A list of references is also appended.

Os Solos do Estado de São Paulo. By José Setzer. Instituto Brasileiro de Geografia e Estatistica, Conselho Nacional de Geografia, Rio de Janeiro, 1949. Pp. 387, figs. 72, diagrams 12, maps 6.

This is a report of a soil survey of the State of São Paulo, Brazil. The work was started in 1935 by Professor Vageler, who continued with it until he left Brazil in 1939. His assistants then completed the job. Some 450 soil profiles were studied and about 1,000 samples of A-horizon material were analyzed. The report gives the parent materials, climate, topography, history of land use, crops, and types of farming. A 9-page summary in English is appended. The bibliography contains 114 references. The illustrations, including both photographs and diagrams, are of considerable interest and value, and the maps give generalized pictures of the geology, climate, and soil.

Wartime Economic Planning in Agriculture. By BELA GOLD. Columbia University Press, New York, 1949. Pp. 594. Price $6.75.

This is number 551 of studies in history, economics, and public law edited by the faculty of political science of Columbia University. It has to do with the mobilization of agriculture, production levels in agriculture, distribution of food supplies, adequacy of measures taken, and conflicting pressures during World War II, with some suggestions on future economic planning. In commenting on production results the author writes:

> With the approach of hostilities, agriculture joined other war industries in the march toward production levels which would surpass all previous peaks, but its pace was slower, the duration of its upsurge shorter and, hence, its accomplishments less extraordinary than were achieved by most of the others. . . . Increases in agricultural production during 1940–45 constituted a substantial contribution to the war effort, but one hardly commensurate with the heroic demands of the emergency.

He then proceeds to analyze the causes for our falling "so seriously short even of feasible potentials." The difficulty is laid largely to the inadequacy of governmental planning agencies and to competing and conflicting interests. The book contains a large amount of highly important data on the production and distribution of agricultural commodities and has considerable value for reference purposes.

THE EDITORS.

INTERNATIONAL CONGRESS OF SOIL SCIENCE TO MEET

The Fourth International Congress of Soil Science will meet at Amsterdam, Netherlands, July 24 to August 1, 1950. Among those listed on the program are Richard Bradfield, C. E. Marshall, H. L. Jensen, T. Wallace, F. E. Bear, C. E. Kellogg, H. H. Bennett, L. Dudley Stamp, R. K. Schofield, L. Gisiger, C. H. Bornebusch, J. H. de Hann, and L. A. Richards. Following the meetings there will be 10 days of excursions to three research centers in the Netherlands and 6 days to three research centers in Belgium. Further information may be obtained from Dr. P. A. Rowaan, 3 Van Hallstraat, Groningen, Netherlands.

TOTAL SURFACE OF CLAYS IN POLAR LIQUIDS AS A CHARACTERISTIC INDEX

R. S. DYAL AND S. B. HENDRICKS

U. S. Department of Agriculture

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Montmorillonite is one of the important components contributing to the cation-exchange capacity and plasticity of soils. Methods for its estimation have been based on x-ray diffraction, chemical analysis for characteristic constituents, cation exchange, and differential thermal analysis. None of these is entirely adequate, but combined use of several methods is rather reliable even though time-consuming. Diffraction methods, which are often used, depend upon the degree of orientation of the layer minerals in the sample. Difficulty is experienced in obtaining either extreme of perfectly or randomly oriented samples.

Montmorillonite and endellite, the hydrated form of halloysite, are the only clay minerals that form definite solvates with polar molecules between the structural layers. Layer hydrates of montmorillonite contain one to possibly four layers of water molecules (4, 7), and conditions cannot necessarily be established for formation of a definite hydrate to the exclusion of others. Ethylene glycol, glycerol, and other polyhydroxylic aliphatic compounds have been shown by Bradley (1) and MacEwan (6) to form two-layer solvates in the presence of excess solvent. These solvates are relatively stable under desiccation or exposure to moist air. Their stabilities and the fact that the separation of the layers is in the region of 17.0 A. make the solvates ideal for identification of montmorillonite by x-ray diffraction. It might be expected that a definite amount of a compound would be required for complete formation of the solvate and that direct estimation of this amount could serve as the basis for an analytical method.

Presence in clays and soils of mixed layer minerals (3, 10) having in part the swelling and base-exchange properties of montmorillonite raises some question as to the type of analysis desired. These minerals cannot readily be identified by x-ray diffraction methods and their poorly defined character has limited complete mineralogical descriptions of finely divided fractions of soils. An analytical method is needed to measure the interlayer swelling irrespective of mineral type. One is proposed here depending upon direct gravimetric determination of ethylene glycol sorption of a sample.

Solvation of clay minerals takes place not only between structural layers where possible but also on external surfaces: measurement of total solvation, therefore, can afford a measure of total surface in polar systems. If the internal surface alone is to be determined, then some estimate must be made of external surface. This can best be done by the Brunauer, Emmett, Teller method (2, 8) of gas sorption using nonpolar compounds. Approximate values of external surface can also be obtained by several other simple methods, as will be described.

In the end, however, greatest interest for soils work might be in the total surface for polar systems, since this would give a measure of interaction with water. The cation-exchange capacities of clay minerals also appear to be approximately determined by the total surface in polar systems.

MATERIALS

Clay minerals of the montmorillonite, micalike (hydrous mica), and kaolin groups were selected, and fractions having apparent diameters of less than 2 μ were separated by sedimentation. The finely divided fraction separated from commerical Wyoming bentonite (Volclay) was used in much of the work on montmorillonite. Observations were also made on a number of bentonite samples selected by the Filtrol Corporation of Los Angeles as representing clays with various swelling characteristics. These were labeled as Randsburg, Blue Itawamba, Chambers, Tehachapi, and Cheto. Kerr and Kulp (5) refer to montmorillonite from Itawamba mine of the Filtrol Company in Itawamba County, Mississippi. They also refer to a montmorillonite from Chambers, Arizona.

Illite separated from a type of shale[1] was used for most of the observations on micalike miners. A carefully separated material from the Ordovician bentonite of Chickamauga Dam, Tennessee; hydrous micas from Evansville, Tennessee, from Thunder Mountain, Nevada, and from Manhattan, Nevada; and a typical sericite from Amelia, Virginia, were also studied.[2] Commercial English china clay, from a large lot that has been extensively studied in this laboratory, served as a reference kaolinite type clay mineral. Halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) was separated from type indianite.[3]

Ethylene glycol was the purified grade of the Eastman Kodak Company. This was used without further treatment in many of the early experiments. In the final work it was redistilled under reduced pressure to eliminate water and a minor impurity of low volatility.

DESORPTION OF ETHYLENE GLYCOL

Changes in the rate of loss of ethylene glycol under conditions of molecular distillation, that is, improbable return of an escaping molecule, from glycol-clay mixtures give an insight into glycol and clay interaction. Measurements were carried out with the arrangement shown in figure 1. A weighed amount of clay, which had been saturated with a particular ion and then dried to constant weight over P_2O_5 at room temperature, was mixed with an approximately equal weight of ethylene glycol. The mixture contained in a shallow weighing dish (2.0 cm. in diameter) was placed on the pan of the Jolly balance housed in a container that could be evacuated. The container was a 12-inch vacuum desiccator with a long glass tube fitted into the top to give room for the Jolly spring. The bottom of the desiccator was covered with a thick layer of anhydrous $CaCl_2$. Evaporation of the glycol was started by evacuating the system to less than 0.1 mm. Hg and was followed by observing a fixed point on the Jolly spring with a Cathetometer. A flat glass was sealed with Canada balsam to the side of the desiccator to facilitate observation.

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[1] Supplied by R. E. Grim of the Illinois State Geological Survey.

[2] These materials were supplied by Clarence Ross of the U. S. Geological Survey.

[3] Collected by Eugene Callahan of the University of Indiana.

Evaporation of ethylene glycol in the presence of hydrogen Randsburg montmorillonite is contrasted in figure 2 with that of the pure liquid in a similar container. Rate of glycol loss in the presence of the clay becomes very slow near 0.25 gm. glycol per gram clay. The montmorillonite complex formed in this way has an interplanar spacing of about 17.1 A., which is the value found by Bradley (1) and MacEwan (6) for the two-layer solvate.

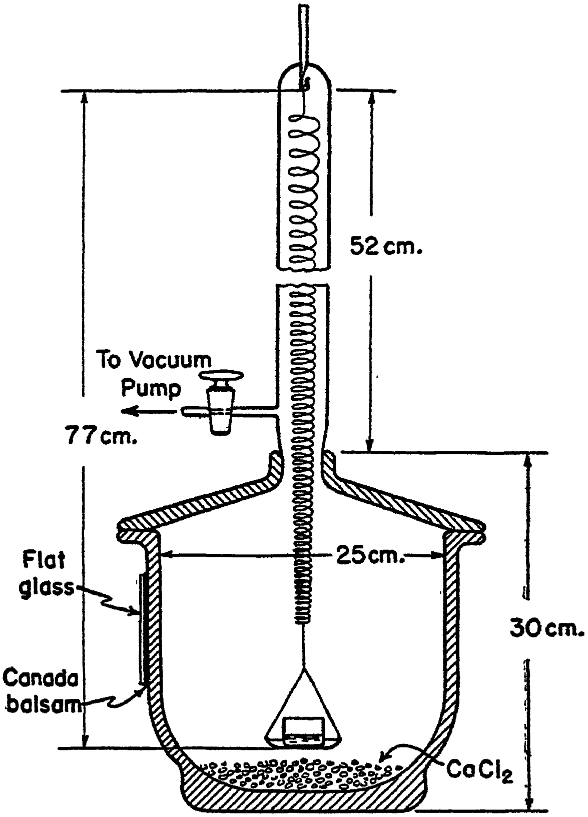

FIG. 1. APPARATUS FOR CONTINUOUS OBSERVATION OF DESORPTION UNDER VACUUM OF ETHYLENE GLYCOL FROM CLAYS

Results obtained with ethylene glycol evaporation in the presence of illite, halloysite, and kaolinite are shown in figures 2 and 3. The various samples were weighed on an analytical balance after 960 minutes to obtain accurate values for residual ethylene glycol. The values for halloysite and kaolinite were 0.020 and 0.019 gm. per gram clay, respectively.

The rate of ethylene glycol loss, either alone or in the presence of a clay,

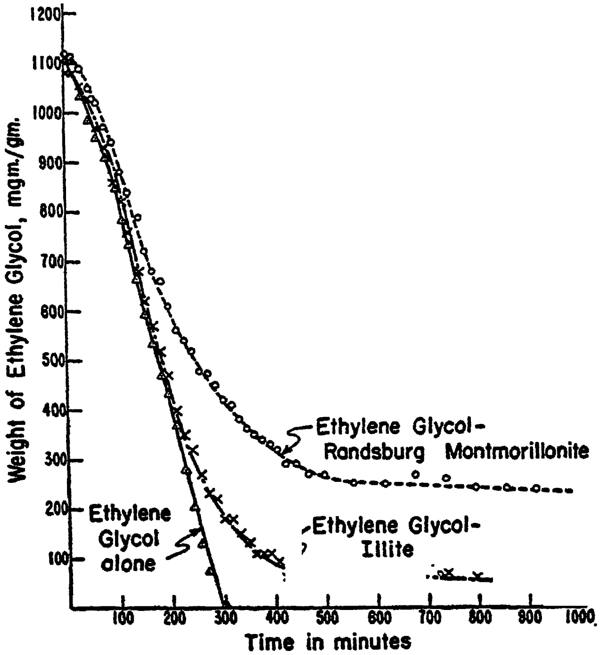

FIG. 2. EVAPORATION OF ETHYLENE GLYCOL FROM RANDSBURG BENTONITE, ILLITE, AND A FREE SURFACE IN A DISH OF 2.0 CM. DIAMETER

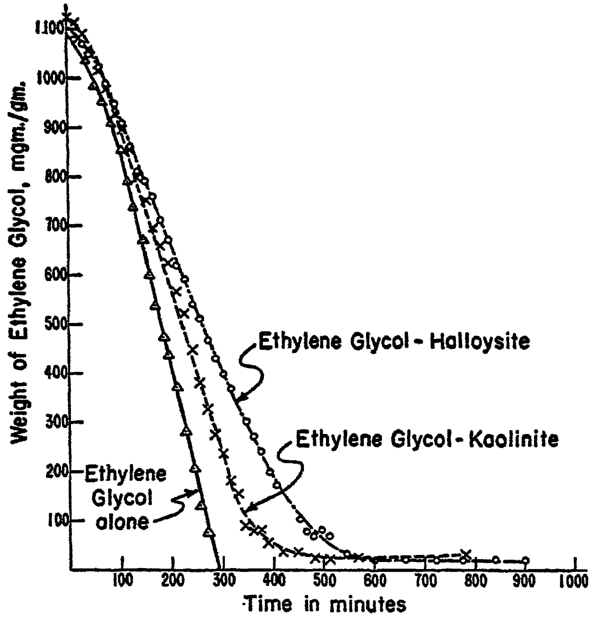

FIG. 3. ETHYLENE GLYCOL EVAPORATION FROM THE KAOLIN MINERALS, HALLOYSITE AND KAOLINITE, CONTRASTED WITH THAT FROM A FREE SURFACE IN A DISH OF 2.0 CM. DIAMETER

naturally depends upon the surface exposed to desiccation. In the presence of clay, diffusion of glycol from the lower portion in a weighing dish to the top of the solid might become limiting. The isothermal loss from the pure liquid should, of course, be predictable if ideal conditions for molecular distillation are established. Under the conditions of these experiments, however, it seemed best to test empirically the rate of loss from several containers of different cross section. Results obtained for hydrogen Wyoming bentonite are shown in figure 4.

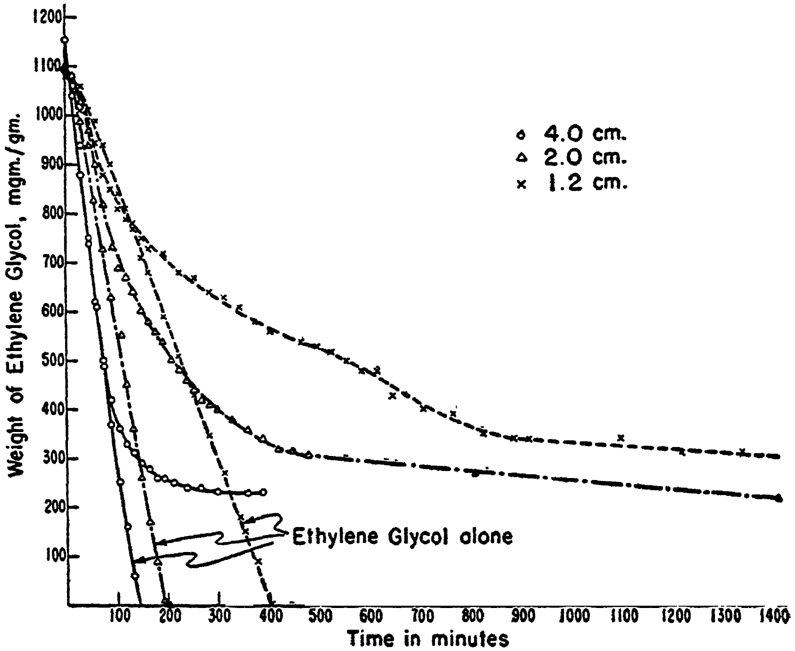

FIG. 4. ETHYLENE GLYCOL EVAPORATION FROM 1.0 GM. OF HYDROGEN WYOMING BENTONITE AND A FREE SURFACE IN WEIGHING DISHES OF DIFFERENT DIAMETERS

EXTERNAL AND INTERNAL SURFACES

External surfaces under nonswelling conditions were measured by the Brunauer, Emmett, and Teller (BET) method (2). These measurements were carried out[4] with ethane at −78°C. (8). The surfaces of the hydrogen Wyoming bentonite, kaolinite, and halloysite measured in this way were 43.9, 28.2, and 44.4 sq. m./gm. respectively after drying at 200°C. The surface of the bentonite showed a variability of about 5 per cent, depending upon the way in which the material was treated during drying.

The total layer face surface area of montmorillonite can be calculated on the basis of a unit cell having a = 5.25 A. and b = 9.20 A. containing one $(\mathrm{Al}_{1.67}\ \mathrm{Mg}_{0.33})\ \mathrm{Si}_4\mathrm{O}_{10}(\mathrm{OH})_2\ \mathrm{H}_{0.33}$ in average composition per face (10). The face area for a unit weight (360 gm.) thus is $5.25 \times 9.20 \times 10^{-16} \times 6.02 \times 10^{23}$ sq. cm. or 2.91×10^5 sq. m. corresponding to 810 sq.m./gm. Variations in composition change this value, but the change would be serious only in the presence of considerable iron in the lattice as in nontronites.

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[4] By R. A. Nelson, formerly of these laboratories.

The external surface for the hydrogen Wyoming bentonite (43.9 sq.m./gm.) is only about 5 per cent of the total face surface area. This external surface, of course, is formed in part of external layer faces as well as side faces. If the individual crystals have a thickness of less than one tenth their lateral dimensions, as is indicated by electron micrographs, then the side face area is less than 20 per cent of the external surface, or about 1 per cent of the layer face surface.

Adsorption upon an external layer face is not equivalent to that on an internal face. In the latter case, the adsorbed glycol on a particular face would be in contact with that on a contiguous face. Complete or partial formation of two layers of ethylene glycol might take place on external faces. In montmorillonite, perfection of the (001) x-ray reflections show that many silicate layers are present in the diffracting unit, that is, the number of external faces is small compared with the number of internal ones.

The preceding considerations afford a basis for estimating the amount of ethylene glycol required for a single surface layer corresponding to two glycol layers between silicate surfaces of montmorillonite. This value is 0.25 gm. glycol on 810 sq. m. of surface or 3.10×10^{-4} gm. glycol per square meter. The corresponding area per glycol molecule is 33×10^{-16} sq. cm., a value consistent with the ethylene glycol molecules lying with CH_2 and OH groups upon the surface as required by Bradley's determination of electron distribution in the layer solvates (1).

If 3.10×10^{-4} gm. glycol per square meter is taken as the quantity necessary for formation of one layer, then the kaolinite and halloysite samples with external surface areas of 28.2 and 44.4 sq.m./gm. would require 0.0088 and 0.0138 gm. ethylene glycol, respectively for single layers. Since about 0.02 gm. glycol is present per gram of clay, a clear-cut conclusion cannot be drawn between presence of single layers, double layers, or possible intermediate values of glycol on the external clay surfaces.

ANALYSIS FOR INTERLAYER SWELLING

The internal surface is the difference between the surface indicated by ethylene glycol retention and the external surface. The ethylene glycol value can best be measured by the Jolly balance procedure. Results given in figures 2 and 3, however, indicate that the rate of loss in weight below the point of change to the lowest rate is very small. With the arrangements used here, involving about 1 gm. of clay and 1 gm. of ethylene glycol in a dish of arbitrary type and arbitrary placement in the desiccator, 16 hours is usually adequate to reach this region. This 16-hour value can be used as a measure of the surface for ethylene glycol retention. A second weighing should be made a number of hours later, say after a total time of 23 hours, as convenient, to establish that the region of lowest rate of loss had been attained or that different times are required. The surface in square meters per gram can be taken as the weight of glycol retained per gram of clay divided by a constant, which might be 3.10×10^{-4}. The value of this constant might be questionable for clays having small internal swelling.

Direct measurement of ethylene glycol retained by the external surface of a substance would be preferred to an independent determination of external surface and an estimate of the amount of glycol retained by a unit area. This implies some method of preventing internal swelling. After several possibilities were tested, attention was devoted to prior heating as a method for suppression of interlayer swelling of montmorillonite in polar liquids.

Results obtained for ethylene glycol retention of several clay minerals heated at various temperatures in air for 4 to 5 hours are listed in table 1. Hydrogen-saturated montmorillonites heated to 500°C. still show interlayer solvation; also, the amount of ethylene glycol adsorbed by the illite has increased. When the clays are heated to 600°C., interlayer swelling is further reduced for the H-montmorillonite, and the surface is within the region indicated by the BET method, that is, same order of magnitude as the values found for kaolinite and halloysite.

Kaolinite, halloysite, and illite following heating undergo some change in ethylene glycol retention. The absolute change, however, is small compared with the retention value for unheated montmorillonite and is not a serious factor limiting the use of heating as the basis for an approximate method.

DETAILED INSTRUCTIONS

Treatment of the several preceding topics makes possible presentation of a detailed method for measuring ethylene glycol retention by clays.

Apparatus: Pyrex vacuum desiccator (12-inch) with porcelain plates. Vacuum pump to reduce pressure to less than 0.1 mm. Hg, analytical balance, and weighing dishes 2.0 cm. in diameter by 2.0 cm. in depth.

Chemicals: $CaCl_2$ anhydrous, P_2O_5, and ethylene glycol purest grade. Redistill the ethylene glycol in vacuum, discarding the first and last 10 per cent of distillate.

Procedure: Separate the fraction of clay or soil less than 2.0 μ in diameter and saturate it with respect to hydrogen, then dry it on a steam bath (there is evidence that this heating might have to be avoided) and grind it to pass 60 mesh. Place about 1.1 gm. in a weighing dish and dry it to constant weight in vacuum ($<$ 0.1 mm.Hg) over P_2O_5. First reduce the pressure to 2 or 3 cm. Hg and after at least 2 hours reduce it to the final value to prevent "boiling" due to escape of air. Heat a separate sample of about 1.2 gm. of the hydrogen-saturated clay at 600°C. for 4 hours.

After the sample has reached constant weight over P_2O_5 or after the heat treatment, weigh accurately, add about 1.0 ml. of redistilled ethylene glycol, and set aside overnight to allow uniform wetting. Then place the weighing dish in the vacuum desiccator above about 500 gm. of anhydrous $CaCl_2$ and evacuate the system to a pressure of less than 0.1 mm. Hg. After 16 hours, introduce dry air into the desiccator, and remove and weigh the sample. Replace the sample, evacuate the desiccator for an additional 7 hours, then weigh the sample again. Six determinations can be made in one desiccator at a time. Replace the $CaCl_2$ or dry it at 250°C. for 24 hours after it has been used to adsorb ethylene glycol from 18 samples.

If the loss in weight between 16 and 23 hours, which times are chosen for convenience of the working day, is less than 0.020 gm., use the 16-hour value for ethylene glycol retention. Performance of the system can be tested by evaporation of ethylene glycol at the rate of at least 1.0 ml. in 8 hours.

TABLE 1

Ethylene glycol retention by various clay minerals after heating in air

CLAY MINERAL	TEMPERATURE OF TREATMENT	ETHYLENE GLYCOL RETENTION		
		16 hrs.	24 hrs.	39 hrs.
	°C.	*gm./gm.*	*gm./gm.*	*gm./gm.*
H-Montmorillonite				
Wyoming	unheated	0.253–0.262	0.236–0.245	
	400	0.153	0.137	0.105
	500	0.056–0.040	0.041	0.028
	600	0.034–0.020	0.019	0.012
Randsburg	unheated	0.240	0.226	
	400	0.147	0.134	0.120
	500	0.044	0.031	0.023
	600	0.008	0.006	0.004
Blue Itawamba	unheated	0.236–0.259	0.214	
	400	0.153	0.129	0.105
	500	0.098	0.079	0.061
	600	0.036	0.027	0.017
Ca-Montmorillonite				
Randsburg	500	0.234	0.219	0.201
Blue Itawamba	unheated	0.244		
	500	0.232	0.211	0.187
La-Montmorillonite				
Wyoming	400	0.291	0.262	0.244
	500	0.264	0.240	0.220
	600	0.248	0.224	0.206
H-Kaolinite	unheated	0.019–0.028	0.015	
	400	0.027	0.018	0.014
	500	0.015–0.010	0.011	0.009
	600	0.011–0.018	0.007	0.006
H-Halloysite	unheated	0.020	0.014	
	400	0.063	0.022	0.015
	500	0.081	0.016	0.011
	600	0.079	0.012	0.011
H-Illite	unheated	0.073–0.060	0.058	0.046
	400	0.086	0.055	0.041
	500	0.098–0.086	0.059	0.037
	600	0.087–0.075	0.047	0.025

The difference between ethylene glycol retention of the unheated and heated clay divided by 3.10×10^{-4} expresses the approximate extent to which the clay has montmorillonite interlayer swelling.

APPLICATION OF THE METHOD

Results for ethylene glycol retention by various clay minerals are shown in table 2. It will be noted that the six montmorillonite samples give similar values, indicative of the solvation of essentially all layers. Ethylene glycol retention by the six micalike clay minerals is smaller and more variable, as would be expected if solvation is largely restricted to external surface. For the specimen from Evansville, Tennessee, the relatively large value of ethylene glycol retention after 24 hours (the more trustworthy period in this case) and the decrease in this value upon heating to 600°C. as well as the medium value of the external surface for ethane adsorption indicate presence of interlayer swelling. This swelling is about 10 per cent of that of montmorillonite and is not unexpectedly great for micalike clay minerals.

TABLE 2

Ethylene glycol retention by various clay minerals previously dried over P_2O_5

CLAY MINERAL	ETHYLENE GLYCOL RETENTION			SURFACE BEFORE HEATING, ETHANE BET
	16 hrs.	24 hrs.	Heated to 600° 23 hrs.	
	gm./gm.	*gm./gm.*	*gm./gm.*	*sq.m./gm.*
H-Montmorillonite				
Wyoming	0.253	0.236	0.019	43.9
Randsburg	0.240	0.226	0.006	51.5
Blue Itawamba	0.236	0.243	0.027	89.8
Tehachapi	0.246	0.223		
Chambers	0.274	0.258		
Cheto	0.289	0.273		
Micalike				
Illite	0.073	0.058	0.058	89.6
Chickamanga Dam	0.059	0.051		
Evansville, Tenn.	0.096	0.074	0.054	53.4
Thunder Mt., Nev.	0.047	0.039	0.024	
Manhattan, Nev.	0.044	0.036	0.035	
Sericite, Amelia, Va.	0.026	0.014		
Kaoline				
Kaolinite	0.019	0.014	0.007	28.2
Halloysite	0.020	0.014	0.012	44.4

Results obtained from mixtures of H-Wyoming bentonite (montmorillonite) and H-kaolinite are shown in figure 5. A linear relationship is found between ethylene glycol retention and percentage of montmorillonite except for the region below 5 per cent. Irregularity in this region might have been a result of using a single desiccator for all ten samples.

Measurements of ethylene glycol retention by the separated clay fractions (2 μ) from the B horizons of several soils now under study in other work on

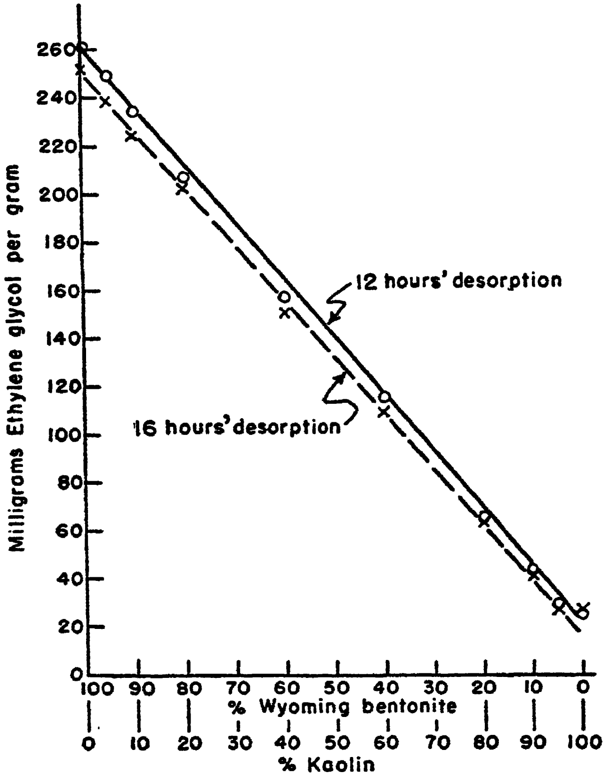

FIG. 5. ETHYLENE GLYCOL RETENTION BY VARIOUS MIXTURES OF KAOLINITE AND MONTMORILLONITE

TABLE 3

Ethylene glycol retention by clays of several soils from upland and river terraces of southern coastal plain

SOIL SERIES AND ION	LAB. NO.	LOCATION	ETHYLENE GLYCOL RETENTION AFTER 24 HOURS		
			Unheated	Heated to 600°C.	For internal swelling
			gm./gm.	*gm./gm.*	*gm./gm.*
H-Ruston	45648	Union Parish, La.	0.042	0.040	0.0
H-Cahaba	45637	Lincoln Parish, La.	0.059	0.055	0.0
H-Leaf	45553	McLennan Co., Texas	0.147	0.078	0.069
H-Boswell	45577	Henderson Co., Texas	0.170	0.087	0.083
Ca-Leaf	45553	McLennan Co., Texas	0.160	0.071	0.089
Ca-Boswell	45577	Henderson Co., Texas	0.175	0.064	0.111

classification are shown in table 3. Two of these, the Ruston and the Cahaba, are essentially free of interlayer swelling. The other two, the Leaf and the Boswell, have about 60 per cent of the ethylene glycol retention of montmorillonite, which is here taken as 0.24 gm. per gram montmorillonite after 24 hours. The amount of ethylene glycol involved in internal swelling is shown in the last column of table 3.

DISCUSSION

The initial purpose of this work was to develop a simple method for quantitative estimation of montmorillonite in clays separated from soils. This objective was realized within its narrow sense by measurement of interlayer swelling which is a property peculiar to montmorillonite among the pure clay minerals. As the work progressed, however, the evidence became overwhelming that an even more fundamental property of clays was being measured. This property was interaction of external as well as swelling surface with polar liquids. Water is, of course, the most important of these liquids, but neither a simple nor an adequate way was conceived for its use.

The property to be measured is the retention by clays under equilibrium conditions of some compound containing predominant hydroxyl groups. Capillarity phenomena are confusing near saturation pressures. At lower pressures, water and some other polar liquids form incomplete solvates. Many glycols, however, form definite montmorillonite solvates having low vapor pressure relative to that of the liquid. The condition thus can be realized of evaporating excess liquid without having an indefinite solvate remaining. Choice of ethylene glycol was based on its reasonable but low volatility in vacuum at room temperature.

Several uncertainties are evident. The amount of ethylene glycol required for surface solvation of montmorillonite is perhaps uncertain by about 6 per cent of its value as a limit, that is, 0.255 ± 0.015 gm. per gram montmorillonite. This is because loss of liquid is continuous. An analysis of the loss curves could lead to a more exact criterion than that of inspection as used, but other uncertainties, such as lack of separation of all layers, did not seem to justify such a procedure. The low total surface of kaolin minerals introduces a greater percentage error into their ethylene glycol retention; in fact, this might be as great as 25 per cent, for example, 0.02 ± 0.005 gm. per gram clay. Measurement for these minerals can be greatly refined, but the approximate value simply obtained meets the present purpose of use in intermediate regions.

Other methods of solvation were tried and discarded. Among these was wetting with ethylene glycol followed by washing with various nonpolar solvents and analysis by periodate oxidation. Adsorption from a saturated vapor and desorption of ethylene glycol at a reduced temperature relative to the sample proved unsatisfactory, possibly because of capillary condensation.

The solvation constant is the desired quantity for clay characterization, but there is interest in the extent of internal solvation, which requires estimation of external surface. Destruction of swelling by heating has inherent dangers. An effort was made to keep the required temperature as low as possible to avoid structural rearrangements. Temperatures of 600°, as used, unfortunately are high enough for decomposition of kaolin minerals. Previous measurements, however, have indicated that the BET values are not greatly changed by decomposition (9). An alternative procedure would be to obtain BET values, but this would be the most arduous part of the procedure in systematic application. A simplified method based upon desorption of toluene and other nonpolar solvents followed with the Jolly balance was attempted but not examined thoroughly.

Figures 2 to 4 show that evaporation of ethylene glycol from clay takes place at nearly the same rate as that from the pure liquid over a considerable region. After disappearance of a liquid surface, this rate, of course, is influenced by the area of the exposed clay and the rate of movement of glycol from lower portions of the clay. In a 4.0-cm. diameter dish containing 1.0 gm. of clay, the rate of loss of glycol deviates from that of the pure liquid, in a similar dish, at about 0.45 gm. per gram montmorillonite. A marked change in rate of glycol loss from kaolinite in a 2.0-cm. dish takes place only below 0.10 gm. per gram clay. These values are of interest in indicating the maximum distance over which the heat of vaporization of a hydroxylic liquid is appreciably influenced by the presence of clay. The distance is less than 5 atomic diameters; this measurement, though crude, is perhaps unique in being trustworthy and can be refined greatly when desired.

SUMMARY

A simple gravimetric method based on retention of ethylene glycol has been developed for measuring total surface, external surface, and, by difference, internal surface for clays in water and other polar systems. A number of clay minerals and several clay fractions of soils were tested by the procedure. The results can be normlaized against montmorillonite and the values obtained used as an index, important for description of soils, that replace in part the need for mineralogical analysis of the clay fraction.

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EFFECT OF VARIOUS LEACHING TREATMENTS ON GROWTH OF ORANGE SEEDLINGS IN OLD CITRUS SOILS[1]

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It is often difficult to grow citrus trees satisfactorily in California soils previously cropped for long periods to orange, lemon, or grapefruit. In greenhouse experiments[3] citrus seedlings made 50 to 175 per cent more growth in soil from areas that had never been cropped to citrus than in that from adjacent old orange and lemon orchards. Ordinary fertilization did not rectify the condition. Heavy treatment of the soil with such fumigants as carbon disulfide, D-D, chloropicrin, and ethylene dichloride usually improved growth of citrus seedlings, and in some cases more than doubled it, but did not increase growth to a point comparable to that in fumigated or untreated noncitrus soil. Since the fumigation treatments markedly altered the microbial population of the soil and yet did not restore its original productive power with respect to citrus, it was decided to try some rather drastic chemical leaching treatments, on the theory that in addition to harmful organisms some kind of a toxin might be accumulating in these old soils and exerting a depressing effect on growth.

EXPERIMENTAL

Experiment 1

Hanford sandy loam was used for the studies reported in this experiment. Soil was obtained from an old citrus grove in which the owner is experiencing difficulty in establishing satisfactory replants. Soil was also obtained from an adjacent garden plot and from several other areas that had never been cropped to citrus. The soils were taken from a depth of 8 to 48 inches.

Two months before planting, the soils were placed in 3-gallon pots and treated as follows:

Leaching treatment	*Procedure*
None (control)	Allowed to stand in greenhouse until crops were planted.
Distilled water	Leached 8 hours a day for 6 weeks with distilled water. Approximately 2 to 3 gallons of water a day leached through each pot. Soil allowed to dry out in pots prior to planting.
Ethyl alcohol	Leached with 6 gallons of 95 per cent ethyl alcohol per pot. More than 5 gallons of alcohol leached through each pot. Soil spread on paper to dry thoroughly; then fertilized, repotted, and planted.

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[2] The author expresses his appreciation to Thomas Beckett and Jarel Ervin for greenhouse assistance, and to H. D. Chapman for helpful suggestions in the course of this work.

[3] Martin, J. P. Effect of fumigation, fertilization, and various other soil treatments on growth of orange seedlings in old citrus soils. *Soil Sci.* 66: 273–288. 1948.

Leaching treatment	*Procedure*
H_2SO_4 pretreatment, calcium saturation	Leached with approximately 6 gallons of 2 per cent H_2SO_4 per pot, with *N* ammonium acetate at pH 7 until the leachate came through at pH 7, and then with *N* $CaCl_2$ until no ammonia was present in the leachate. Excess chloride was leached out with distilled water. Soil allowed to dry out in pots prior to planting.
KOH pretreatment, calcium saturation	Leached with approximately 4 gallons of 2 per cent KOH per pot, then converted into a calcium soil as in the acid (H_2SO_4) treatment above. Soil allowed to dry out in pots prior to planting.
NH_4Cl pretreatment, calcium saturation	Leached with *N* NH_4Cl solution at pH 4 until the leachate came through unchanged; then converted into a calcium soil as in the acid (H_2SO_4) treatment above. Soil allowed to dry out in pots prior to planting.

Just prior to planting, each pot of soil received the following fertilizers:

Material	*Grams per pot*
Ammonium nitrate, C.P.	4.0
Treble superphosphate, commercial	2.0
Potassium chloride, C.P.	0.7
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$), C.P.	0.4
Copper sulfate ($CuSO_4 \cdot 5H_2O$), C.P.	0.028
Boric acid, C.P.	0.006
Manganese sulfate ($MnSO_4 \cdot 4H_2O$), C.P.	0.084
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$), C.P.	0.028

The phosphate was mixed with the soil, and the other fertilizers were added in solution.

The leaching treatments were replicated nine times for each soil. Three pots from each treatment and from each soil were planted respectively to sweet orange seedlings, sour orange seedlings, and tomato plants, two plants being placed in each pot. Citrus seedlings selected for size and vigor were planted bare-root[4] and grown for approximately 8 months. Tomato plants were transplanted from flats into the pots and grown approximately 6 weeks. All cultures were watered with distilled water.

The effects of the various leaching treatments on growth of sweet orange seedlings are shown in table 1. There was no significant variation in top growth between the treatments in the *noncitrus* soil. In this soil, however, growth was 80 per cent greater than in the old citrus control soil. All treatments except leaching with distilled water significantly increased top growth in the old citrus soil. The H_2SO_4 and KOH treatments completely eliminated the inhibiting factors. Growth of seedlings in soil receiving these treatments was equal to that in the noncitrus soil. The effects of the treatments on sweet orange root growth were approximately the same as on top growth.

Table 2 records the results of the leaching procedures on the growth of sour orange seedlings. All treatments except leaching with distilled water and alcohol

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[4] Roots of seedlings washed free of soil before planting.

TABLE 1

Effects of various leaching treatments on growth of sweet orange seedlings in old citrus and noncitrus Hanford sandy loam soils

LEACHING TREATMENT AND POT*	PLANT GROWTH PER POT									
	Tops					Roots				
	Old citrus soil	Difference due to treatment	Noncitrus soil	Difference due to treatment	Increase or decrease, noncitrus over old citrus soil	Old citrus soil	Difference due to treatment	Noncitrus soil	Difference due to treatment	Increase or decrease, noncitrus over old citrus soil
	gm.†	*per cent*	*gm.*†	*per cent*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*per cent*
None (control)										
A	31		51			9		17		
B	26		54			11		21		
C	32		56			10		18		
Av	30	0	54	0	80	10	0	19	0	90
Distilled water										
A	31		57			11		19		
B	38		58			13		18		
C	34		54			12		22		
Av	34	13	56	4	65	12	20	20	5	66
Ethyl alcohol										
A	41		48			15		16		
B	48		58			19		22		
C	49		55			16		18		
Av	46	53	54	0	17	17	70	19	0	12
H_2SO_4 pretreatment, Ca saturation										
A	50		50			17		18		
B	56		58			21		18		
C	55		50			21		21		
Av	54	80	52	−4	−4	20	110	19	0	−5
KOH pretreatment, Ca saturation										
A	56		56			22		21		
B	55		55			25		19		
C	50		52			17		24		
Av	54	80	54	0	0	21	110	21	10	0
NH_4Cl pretreatment, Ca saturation										
A	46		48			15		16		
B	46		54			17		21		
C	40		53			14		17		
Av	44	47	52	−4	18	15	50	18	−5	20

TABLE 2

Effect of various leaching treatments on growth of sour orange seedlings in old citrus and noncitrus Hanford sandy loam soils

LEACHING TREATMENT*	AVERAGE PLANT GROWTH PER POT									
	Tops					Roots				
	Old citrus soil	Difference due to treatment	Non-citrus soil	Difference due to treatment	Increase or decrease, noncitrus over old citrus soil	Old citrus soil	Difference due to treatment	Non-citrus soil	Difference due to treatment	Increase or decrease, noncitrus over old citrus soil
	gm.†	*per cent*	*gm.*†	*per cent*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*per cent*
None (control)	32	0	56	0	75	12	0	21	0	75
Distilled water	34	6	58	3	71	13	8	19	−9	46
Ethyl alcohol	36	12	46	−18	28	13	8	17	−19	31
H_2SO_4 pretreatment, calcium saturation	42	31	46	−18	9	19	58	18	−14	−5
KOH pretreatment, calcium saturation	46	44	46	−18	0	22	83	21	0	−5
NH_4Cl pretreatment, calcium saturation	39	22	50	−11	28	14	17	18	−14	28

* All pots received N, P, K, Mg, B, Cu, Zn, and Mn fertilizers.

† According to an analysis of variance, a difference of 5 gm. is significant; 7 gm., highly significant.

TABLE 3

Effect of various leaching treatments on growth of tomato plants in old citrus and noncitrus Hanford sandy loam soils

LEACHING TREATMENT*	AVERAGE PLANT TOP GROWTH PER POT				
	Old citrus soil	Difference due to treatment	Noncitrus soil	Difference due to treatment	Increase or decrease noncitrus over old citrus soil
	gm.	*per cent*	*gm.*	*per cent*	*per cent*
None (control)	34	0	31	0	−9
Distilled water	28	−18	25	−19	−11
Ethyl alcohol	25	−26	23	−26	−8
H_2SO_4 pretreatment calcium saturation	21	−38	21	−32	0
KOH pretreatment, calcium saturation	24	−29	24	−22	0
NH_4Cl pretreatment, calcium saturation	27	−21	26	−26	−3

* All pots received N, P, K, Mg, B, Cu, Zn, and Mn fertilizers.

significantly increased growth in the old citrus soil and all slightly decreased growth in the noncitrus soil. Growth was just as great, however, in the old citrus soil leached with the H_2SO_4 and the KOH as in the noncitrus soil which received the same treatment.

Tomato plants (table 3) made slightly better growth in the old citrus soil control than in the noncitrus control. All the leaching treatments reduced growth.

Experiment 2

In view of the results of the H_2SO_4 and KOH leaching procedures on growth of orange seedlings, the acid treatment was repeated on old citrus soil made even more unfavorable to growth of citrus by previous cropping to sour orange seedlings in the greenhouse for 9 months. Data not reported in this paper indicated that complete saturation of the soil colloids with calcium was largely responsible for reduced growth of sour orange seedlings in noncitrus soil. For this reason, after acid pretreatment, a portion of the soil was saturated with calcium; other portions were saturated with magnesium, potassium, and hydrogen, respectively. The soils were then combined in the following proportions: 66 per cent calcium soil, 20 per cent magnesium, 7 per cent potassium, and 7 per cent hydrogen soil. For comparison, both treated and untreated old citrus soils were fumigated with 12 ml. CS_2 per pot, and three additional noncitrus soils were used. Tomato plants also were grown in the old citrus and noncitrus control soils. All treatments were replicated five times, and two seedlings were planted in each pot.

TABLE 4

Effect of various leaching treatments and soil fumigation on growth of sour orange seedlings in old citrus soils previously cropped to sour orange seedlings for 9 months in the greenhouse

SOIL AND TREATMENT*	AVERAGE PLANT GROWTH PER POT			GROWTH RATING (NONCITRUS CONTROL = 100)
	Roots	Tops	Total	
	gm.†	*gm.*‡	*gm.*	*per cent*
Hanford sandy loam:				
Noncitrus (control)	27	66	93	100
Old citrus (control)	6	12	18	19
Old citrus fumigated with CS_2	9	16	25	27
Old citrus H_2SO_4-pretreated and variously saturated§	28	65	93	100
Old citrus (same as above) fumigated with CS_2	28	64	92	99
Yolo sandy loam (noncitrus)	31	61	92	99
Romona clay loam (noncitrus)	30	59	89	96
Meloland clay loam (noncitrus)	31	63	94	101

* All pots received N, P, K, Mg. B, Cu, Zn, and Mn fertilizers.

† Difference of 4 gm., significant; 5 gm., highly significant.

‡ Difference of 7 gm., significant; 10 gm., highly significant.

§ Cation saturation: 66 per cent calcium, 20 per cent magnesium, 7 per cent potassium, and 7 per cent hydrogen.

Results are presented in table 4 and in figures 1 and 2. The seedlings in the noncitrus control soil made more than five times the growth of those in the old citrus control. Fumigation of the old soil increased growth by approximately one third. According to statistical analysis of the entire experiment, this increase was not significant, but on the basis of the results from the control and fumiga-

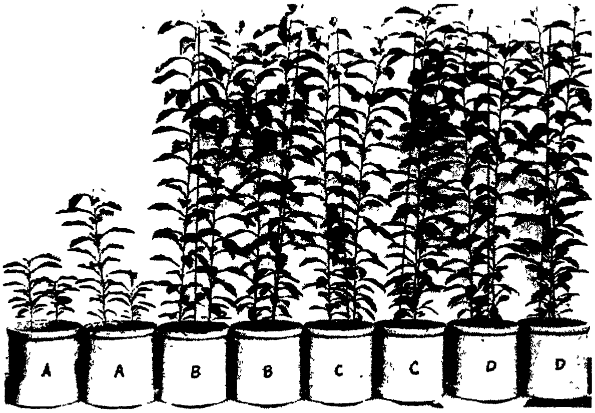

FIG. 1. EFFECT OF LEACHING SOIL WITH 2 PER CENT H_2SO_4 ON GROWTH OF SOUR ORANGE SEEDLINGS

A, Old citrus soil obtained from a citrus grove near Fullerton, California, and cropped to sour orange seedlings in the greenhouse for 9 months before planting; B, same soil leached with 2 per cent H_2SO_4, the leaching followed by saturation of the soil colloids with 66 per cent Ca, 20 per cent Mg, 7 per cent K, and 7 per cent H; C, same soil treated as in B and also fumigated with 12 ml. CS_2 per pot; D, noncitrus soil obtained from a garden plot adacent to old citrus orchard.

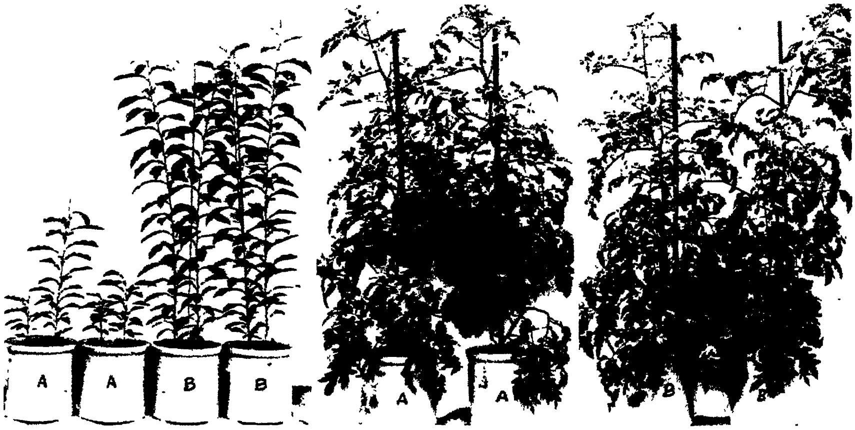

FIG. 2. SOUR ORANGE SEEDLINGS (LEFT) AND TOMATO PLANTS (RIGHT) GROWING IN (A) SOIL OBTAINED FROM AN OLD CITRUS ORCHARD AND CROPPED TO SOUR ORANGE SEEDLINGS FOR 9 MONTHS IN THE GREENHOUSE BEFORE PLANTING, AND IN (B) SOIL OBTAINED FROM AN ADJACENT GARDEN PLOT NEVER BEFORE PLANTED TO CITRUS

tion pots alone, the increase was significant. The acid-leaching process, in addition to the combining of various calcium, magnesium, potassium, and hydrogen fractions to make the soil 66 per cent calcium-saturated, 20 per cent magnesium-saturated, 7 per cent potassium-saturated and 7 per cent hydrogen-saturated (see table 4), however, completely overcame the growth-retarding factors in the old soil. Fumigation of the leached soil had no effect on growth of seedlings. The total weights of seedlings in the three additional noncitrus soils were approximately the same as in the noncitrus control soil.

TABLE 5

Effect of various leaching treatments on growth of sweet orange seedlings in sand previously cropped to sour or sweet orange seedlings for 18 months

CULTURE*	DRY WEIGHT OF 5 PLANTS	GROWTH RATING (FRESH SAND CONTROL = 100)
	gm.	*per cent*
Fresh sand control (no prior cropping or treatment)	36	100
Fresh sand, watered weekly with 500 ml. of leachings from old sour orange cultures	24	66
Sand previous cropped to sour orange seedlings	—†	—†
Sand previously cropped to sour orange seedlings, then leached with approximately 25 gallons distilled water per 3-gallon pot	12	33
Sand previously cropped to sour orange seedlings, then leached with 5 gallons 2 per cent H_2SO_4, followed by 25 gallons distilled water per 3-gallon pot	34	94
Fresh sand watered weekly with 500 ml. of leachings from old sweet-orange cultures	25	69
Sand previously cropped to sweet orange seedlings	16	44
Sand previously cropped to sweet orange seedlings, then leached with approximately 25 gallons of distilled water per 3-gallon pot	29	80
Sand previously cropped to sweet orange seedlings, then leached with 5 gallons of 2 per cent H_2SO_4, followed by 25 gallons of distilled water per 3-gallon pot	41	111

* All cultures watered with 500 ml. of nutrient solution once each week.

† All plants died.

Tomato plants (fig. 2) grew just as well in the old citrus control soil as in the noncitrus control soil. The average dry weight of the tops per pot was 141 gm. and 143 gm. in the old citrus and noncitrus soils, respectively.

Experiment 3

For this study, something similar to a synthetic old citrus soil was made by cropping medium quartz sand in 3-gallon pots to sour or sweet orange seedlings for 18 months. Approximately once a month during the initial cropping period each pot of sand was given an application of nutrient solution containing both major and minor elements.

Two months prior to use, the cultures were leached with approximately 2 to 3 gallons of distilled water per pot and then given a small application of calcium nitrate. The orange seedlings (tops and roots) were then removed, and part of the sand from the original 3-gallon containers was leached, as indicated in table 5. The leached and unleached sand from the original containers, and fresh sand, for comparative purposes, were placed in 1-gallon pots. Each treatment was replicated five times, and only one seedling was planted in each pot. Details of the treatments and their effects on growth of sweet orange seedlings are shown in table 5.

Cropping of sand to sour or sweet orange seedlings for 18 months greatly retarded the growth of a second planting of sweet orange seedlings. Weekly watering of fresh sand cultures of sweet orange seedlings with leachings from old sand cultures reduced growth by approximately a third. Leaching of previously cropped sand with distilled water increased growth of seedlings; leaching with H_2SO_4, followed by distilled water, produced growth comparable to that obtained in the fresh sand. The roots of the seedlings in these two treatments appeared healthy; those in the other treatments showed evidence of decay of some of the feeder roots. Previous cropping of sand to sour orange seedlings had a greater retarding effect on subsequent growth of sweet orange seedlings than did previous cropping to sweet orange seedlings.

DISCUSSION

Leaching of old citrus soil with rather large amounts of distilled water, before planting, did not significantly improve growth of sour or sweet orange seedlings. Similar leaching of sand previously cropped to citrus improved growth of orange seedlings slightly. Leaching of soil with alcohol or with a N solution of NH_4Cl, followed by saturation of the soil colloids with calcium, increased growth of orange seedlings in old citrus soil but did not restore the soil to its original productive state. Pretreatment with 2 per cent H_2SO_4 or 2 per cent KOH, followed by saturation with calcium, completely overcame the retarding effect of old citrus soil on growth of citrus seedlings.

The main theories advanced to explain the retarding effect of old citrus soils on the growth of replants are: (a) *nutritional deficiency*, (b) *nutrient unbalance or excess*, (c) *deterioration of soil structure*, (d) *unfavorable microbial population of soil*, and (e) *accumulation of a toxic substance.*

In the present studies all soil cultures were fertilized with both major and minor nutrients. In previous studies orange seedlings in old citrus soils did not respond to additions of any nutrients except nitrogen. Other plants such as tomatoes grow well in old citrus soils. If some element not included in those added were lacking in the soil, the drastic leaching procedures with various chemicals including relatively strong acid and base, followed by distilled water, would probably further deplete the supply of such a nutrient. In light of the previous experiments and the stimulating effect of the present treatments, it appears very unlikely that a nutritional deficiency is responsible for the reduced growth of citrus.

If the reduced growth of citrus in old citrus soils were caused by an unbalanced nutritional condition or by an excess of some inorganic material in the soil, leaching with distilled water or salt solution might, to some degree at least, alleviate the condition. Although pretreatment with ammonium chloride, followed by saturation of the soil colloids with calcium, improved growth, it did not return it to the status of that in soil never before cropped to citrus. In the greenhouse a noncitrus soil was made very unfavorable to the growth of citrus seedlings by cropping it to orange seedlings for 18 months. Only a small amount of ammonium nitrate was added to the soil. The pots were watered with distilled water. It is improbable that an excess of some element would build up in the soil under these conditions. Furthermore, other plants such as tomatoes grow well in old citrus soils. The evidence therefore does not support the theory of nutritional unbalance as a primary factor.

The depressing effect of old citrus soils on growth of replants occurs in very sandy soils as well as in medium and heavy-textured soils. Cultural practices which tend to cause deterioration of soil structure in citrus groves are also operative in noncitrus agriculture; yet soil from avocado or walnut groves will support the growth of vigorous citrus trees. This, together with the fact that the depressive effect is manifest even after the soil is removed from the field and handled in such a manner as to alter its structural condition, suggests that structural deterioration is not a primary factor.

Previous studies have indicated that detrimental microorganisms are at least partly responsible for reduced growth of citrus in old citrus soils.[5] Nematodes and fungi are found in decaying citrus feeder roots. Heavy fumigation of old citrus soil destroys the nematodes, reduces or eliminates root decay, greatly alters the microbial population of the soil, and usually increases growth of citrus seedlings slightly to moderately. The acid- and base-leaching treatments in this study exerted an effect on the microbial population of the soil similar to that of a heavy soil fumigation treatment: the nematodes were killed and the fungi were initially destroyed, although later a population of fungi developed which consisted of fewer species, and in many pots different species, than were present in the original soil. But whereas the fumigation treatments did not restore growth of citrus seedlings in old citrus soils to the status of that in noncitrus soils, the acid- and base-leaching treatments did.

It is possible that fumigation treatments may exert certain side effects that are detrimental to citrus growth. It is known, for example, that soil fumigation increases the concentration of a number of trace elements in the soil solution. In numerous fumigation studies, however, noncitrus soils obtained from areas adjacent to the old citrus orchards from which soils were obtained, were fumigated in exactly the same manner as the old citrus soils. Fumigation of these soils in some cases slightly decreased and in others slightly increased growth of seedlings; in still others it had no effect. In all instances growth was much better in the fumigated noncitrus soils than in the fumigated old citrus soils. These results cast doubt on the possibility that the fumigation treatments exerted any very great depressive influence. It seems to the author, therefore, that the most reasonable explanation of the results obtained is that, in addition to detrimental organisms, there is an organic toxic material present in the soil. Such a hypothetical toxic substance could be built up slowly in the soil by excretion from the citrus roots, or it could be produced by microorganisms growing on root surfaces or on dead root material.

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[5] Martin, J. P. Fungus flora of some California soils in relation to slow decline of citrus trees. *Soil Sci. Soc. Amer. Proc.* (1947) 12:209–214. 1948. Thomas, E. E. The citrus nematode, *Tylenchulus semipenitrans*. *Calif. Agr. Exp. Sta. Tech. Paper* 2: 1–34. 1923.

If an organic toxic material is one of the factors causing poor growth of citrus in old citrus soils, it is apparently specific for citrus, is not readily leached out of soil by water, is not a replaceable cation, is not completely removed from the soil by ethyl alcohol, but is either soluble in, or destroyed by, sufficiently strong acid or base solutions, and is resistant to attack or is only slowly broken down by microorganism. More work will be required to confirm or disprove this hypothesis, but it seems to agree better than any other with the experimental results obtained.

Results with citrus seedlings in sand cultures were similar to those of Mader[6] in his work with chrysanthemums and roses in sand media.

SUMMARY

On the assumption that a toxic substance is partly responsible for reduced growth of citrus trees in soils previously cropped to the same plant for long periods, experiments were conducted to determine whether soil leaching with various materials would overcome this growth-retarding effect.

Leaching with rather large amounts of distilled water before planting did not significantly improve growth of sour or sweet orange seedlings in old citrus soils. Similar leaching of sand previously cropped to citrus seedlings improved growth of orange seedlings slightly. Fumigation and leaching of old citrus soil with ethyl alcohol and a N solution of ammonium chloride at pH 4, followed by saturation of the soil colloids with calcium, increased growth but did not return it to the status of that in noncitrus soil. Leaching with 2 per cent H_2SO_4 or with 2 per cent KOH, followed by saturation of the soil colloids with calcium or a combination of calcium, magnesium, potassium, and hydrogen, completely overcame the growth-retarding factors in old citrus soil. Similar results were obtained with sand cultures.

Results support the hypothesis that, in addition to detrimental organisms, a toxic material gradually accumulates in soil which is continuously cropped to citrus for long periods. This hypothetical material is toxic to citrus but not to other plants such as tomatoes and avocados; it is either insoluble in water or is absorbed by the soil and held against leaching with distilled water; it is apparently not absorbed as a replaceable base; and it is apparently destroyed by, or is soluble in, relatively strong acid or base solutions.

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INFLUENCE OF CULTIVATION AND WEED KILLERS ON SOIL STRUCTURE AND CROP YIELD[1]

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Weed killers not only should control the weed population but they also should indirectly tend to have a beneficial effect on the structure of soils. Since the soils will not have to be cultivated, or at least not cultivated so frequently, less organic matter should be lost by oxidation. Thus soil structure should be improved and crop yields increased. Should one or two applications of weed killers be adequate for the control of weeds, the number of times heavy machinery is run over the ground will be materially reduced. It is believed that these two factors, among others, will tend to improve or at least maintain a *status quo* of soil structure.

Observations suggest that structure has more influence on the productivity of the soil than formerly was believed. Some work on the effect of cultivation on soil physical properties has been reported (5, 10).

Anderson *et al.* (1)[2] reported no decrease in field corn yields where weeds were controlled by 2,4-D without cultivation. Dearborn[3] has presented evidence that sweet corn yields are greater where applications of 2,4-D and cultivation are combined in controlling weeds.

The purpose of this experiment was to study the indirect effect of synthetic weed killers on soil physical properties and the effect this may have on crop yield in comparison with the usual cultivation methods. This paper is a report of the first year's results.

MATERIALS AND METHODS

Two randomized experiments were set up on Cheshire loam at the station's Mount Carmel Farm to test the effect of weed killers on soil structure. Plots 12 by 24 feet (0.165 A.) were used. A hybrid field corn (Connecticut 520) and Chantenay red cored carrots were the crops used. The corn rows were spaced 36 inches apart, and the carrots, 18 inches.

On half the plots, an 8-16-8 fertilizer was applied at a rate of 1,200 pounds per acre. On the other half, 8-16-8 fertilizer was applied at the rate of 600 pounds and barnyard manure at 20 tons per acre. The manure was applied to determine the effect of added organic matter on soil physical properties. Each treatment was replicated five times. The following experiment was laid out: 1. Pre-emergence control of weeds in corn with 2,4-D; 2. Control of weeds in corn with flame cultivation; 3. Control of weeds in carrots with an oil spray; 4. Control of weeds in corn and carrots by ordinary cultivation methods.

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[1] Contribution from the department of soils, Connecticut Agricultural Experiment Station, New Haven, Conn. Part of this material was presented at the Soil Science Society of America meetings, Milwaukee, Wis., October 24–28, 1949. Grateful acknowledgment is made to D. B. Downs for assistance in the field and laboratory work and to C. I. Bliss for advice on statistical analysis.

[2] Wolf, D. E., Anderson, J. C., and Garrison, C. S. Three years' results on pre-emergence in corn with 2,4-D. *Proc. N.E. States Weed Control Conf.* 1949: 151–154. 1949. (Mimeographed.)

[3] Dearborn, C. H. Productivity of cultivated and uncultivated Golden Cross Bantom sweet corn weeded with post-emergence sprays of 2,4-D. *Proc. N. E. States Weed Control Conf.* 1949: 69–72. 1949. (Mimeographed.)

Corn and carrots were planted May 26, and excellent stands were obtained. The corn emerged on the sixth day.

For treatment 1, the sodium salt of 2,4-D was applied at $1\frac{1}{2}$ pounds per acre as a spray 5 days after planting and again 45 days later. These plots were not cultivated at any time.

For treatment 2, weeds were flamed with a small hand apparatus 6 days after the corn was planted, 26 days later, and again 50 days after the first flaming. These plots were cultivated once immediately after the last flaming.

For treatment 3, the plots were sprayed, when the carrots were about $1\frac{1}{2}$ inches high, at the rate of 75 to 80 gallons of oil (Varsol) per acre. These plots received no cultivation, nor were any weeds pulled by hand.

The plots of treatment 4 were cultivated three times: the corn, 21, 34, and 50 days after planting; and the carrots 21, 34, and 56 days after planting. The corn plots also were hoed four times. The carrot plots were hand-weeded soon after each cultivation.

A Fordson tractor equipped with two-row cultivation equipment was used for cultivating the carrots; for corn, a John Deere Model B tractor equipped with a two-row cultivator was used. At no time were cultural operations carried on when the soils were wet.

To observe the effect of cultivation and of packing of the soil by the tractor, undisturbed soil samples at depths of 0–2, 4–6, 6–8, and 12–14 inches were taken. In addition, samples for comparison were taken in an experimental orchard adjacent to the plots. The samples were taken about 5 feet from the trunk of a tree to insure that the area sampled had not been run over by a spray rig. The orchard had been in bluegrass sod for 12 years. Samples were also taken in the alleys between plot blocks. These alleys were used for turn-around areas for the tractor during cultivation. The samples were taken with an apparatus similar to that described by Lutz (8). The sampling cylinders were $2\frac{5}{16}$ inches high and $2\frac{7}{8}$ inches in diameter, having a volume of 250 ml. For convenience, the height of the cylinders will be referred to as 2 inches.

In the cultivated plots one sampling was made in the area traveled over by the rear tractor wheel, and another sample was taken in the untraveled areas between hills in the row. The experiment was planned so that the rear tractor wheel ran between the same rows each cultivation. For a two-row cultivator, the rear tractor wheel goes between the same rows twice when four rows are cultivated. Since the plots were cultivated three times, this means that the rear tractor wheel passed over the same ground six times. In the 2,4-D and oil-spray plots, equivalent areas were sampled.

Measurements of volume weight (2) and pore-space relationships (total, macroporosity, and microporosity[4]) were made on the core samples. Field-moisture percentages of the soil cores were calculated in the usual manner (tables 2 and 4). Percentage saturation of pore space was determined by a modification of the Leamer and Shaw technique (7) similar to that described by McHenry and Newell (9). Large circular porous ceramic plates[5] were used in place of the Leamer and Shaw type of tension table. The core samples were placed in firm contact on the ceramic plates and saturated by capillarity for 20 hours, and placed under 40 cm. tension of water for 18 hours.

WEATHER CONDITIONS

During May, almost twice as much rain as the average fell; and April and June rains were above the 1932–1947 average (table 1). An unusual number of the rains were of high intensity.

TABLE 1

Weather data for growing season, Mt. Carmel Farm, Connecticut Agricultural Experiment Station

JUNE

*Rainfall, inches**

1948..	..	5.68	7.19	4.49	2.85	3.25	0.51	2.46
1932–1947 Average.		4.04	3.93	4.31	3.24	4.04	4.83	3.23

Mean maximum temperature, °F.†

1948..........	..	55.0	63.5	73.6	81.0	80.8	75.8	63.2
1873–1947 Average ..		55.6	67.2	75.8	80.7	78.8	72.8	62.4

* Data courtesy B. W. McFarland, Connecticut Agricultural Experiment Station.
† Data courtesy Weather Bureau, U. S. Dept. of Commerce, New Haven, Conn.

In contrast, not only was total precipitation for July and August below normal, but 42 per cent of the rain for July and 78 per cent for August fell in one rain in each of those months. The September rainfall was less than 11 per cent of the previous 16-year average. In addition, July, August, and September were unusually hot (table 1): the mean maximum monthly temperature averaged 0.3, 2.0, and 3.0°F. above the 1873–1947 average.

RESULTS

Corn

Growth. Unusual weather during the growing season gave unexpected results. Consequently, yields for corn were low. The heavy rains that fell packed the

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[4] In this paper, the terms "micropores" and "macropores" are used for capillary and noncapillary pores, respectively.

[5] Porous ceramic plates, No. K939, 12-inch diameter, were obtained from the General Ceramic and Steatite Corporation, Keasbey, New Jersey.

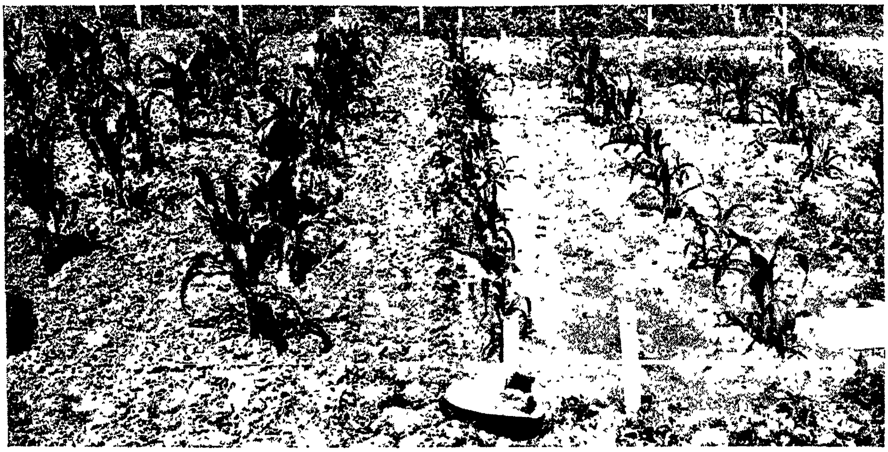

FIG. 1. APPEARANCE OF PLOTS ON JULY 2, 1948, SHOWING SOIL-CRUSTING ON 2,4-D UNCULTIVATED PLOTS AT RIGHT. THE CORN IS LIGHTER GREEN, SMALLER, AND LESS VIGOROUS THAN THAT ON THE CULTIVATED PLOTS AT THE LEFT

Both plots received the same mineral fertilizer treatment.

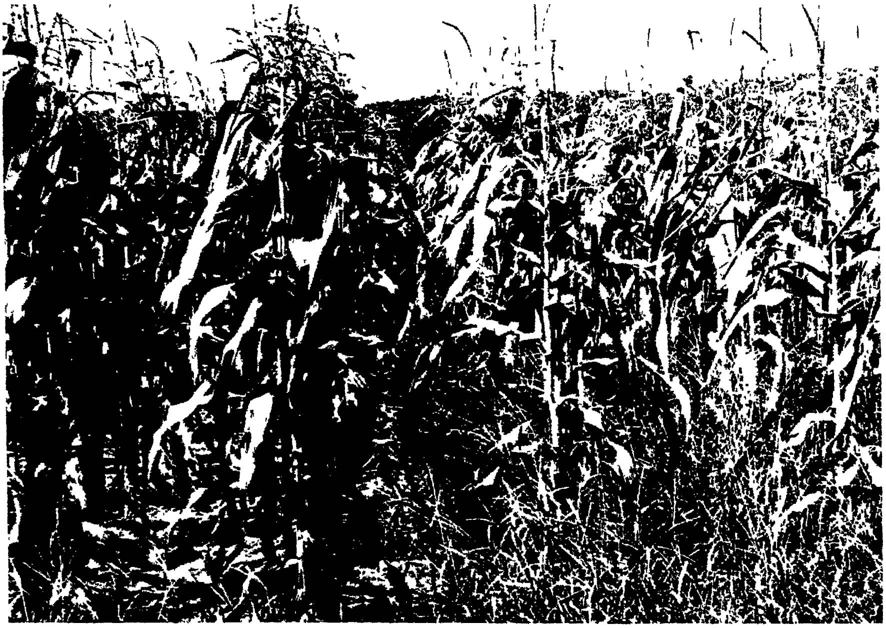

FIG. 2. CULTIVATED (LEFT) AND 2,4-D-TREATED (RIGHT) CORN PLOTS, AUGUST 29, 1948

Note the darker green color, thicker stalks, greater height, and more luxuriant foliage of the corn in the cultivated plot. The cultivated plot is virtually weed-free as against foxtail and crabgrass in the 2,4-D plot. Both plots received mineral and organic (barnyard manure) fertilizers.

ground and, combined with the hot dry weather that followed, formed a hard crust on the soil surface. The result was indirect injury in the 2,4-D plots. Evidently this crust did not allow free circulation of air into the soil, setting up reducing conditions, and resulted in a decrease in the production of nitrates by soil organisms.

In the 2,4-D and flame-cultivated plots, growth of blue-green algae was observed on the soil surface for more than a month after planting. This is further evidence that the soil surface was kept wet and poorly aerated, which was probably due to the soil crust and high rainfall.

At first, growth of all the corn was about the same and all of it had a good green color. Differences started to show up after the corn was more than a foot tall (fig. 1). Height measurements of the corn 50 days after planting gives an index its growth. The 2,4-D-treated corn averaged about 3½ inches shorter than the cultivated corn, and the flame-cultivated corn was about 7 inches shorter. Evidently both the initial noncultivation and the injury by flaming exerted retarding growth effects on the flame-cultivated corn.

No data were obtained on soil nitrate production, but the 2,4-D-treated corn showed definite nitrogen-deficiency symptoms (3, 6) in contrast to the dark green color of the cultivated corn. This nitrogen deficiency showed up early while the 2,4-D plots were free of weeds. The flame-cultivated corn was also lighter green than the cultivated corn but the difference was not nearly so pronounced as in the 2,4-D-treated plots. Figure 1 also shows the crust-like dense surface of the noncultivated (2,4-D plots) corn in comparison with the loose, well-aerated condition of the cultivated corn.

During the dry weather that followed the exceptionally wet spring, the cultivated corn stood the drought best. It remained green longer and showed less evidence of "firing" of the lower leaves and nitrogen deficiency than the others. The flamed corn withstood the drought better than the 2,4-D-treated corn.

Table 2 shows that the cultivated plots had the least soil moisture at the time of sampling, followed in order by the flame-cultivated and the 2,4-D-treated plots. This holds true especially for the 0–2-inch depth and even when comparisons are made between the areas run over by the rear tractor wheel. Averaging the data for the 0–2-, 4–6-, and 6–8-depths brings out these same relationships, but they are less pronounced when the 12–14-inch depth is included. The high amount of moisture in the surface 2 inches of sod is interesting in comparison with the other plots.

The impossibility of taking all core samples the same day adds to the variability of the results, especially for the surface 2 inches. Since the plots were randomized, the samplings of the various treatments were distributed over the sampling period. Also, sampling was done in late October and early November when changes in soil moisture are less rapid than during the summer months.

The soil moisture differences were in reverse order of yields for the plots. The cultivated plots yielded 61.5 bushels per acre with organic and mineral fertilizers and 63.9 bushels with mineral fertilizer; the corresponding yields were 52.7 and 55 for the flame-cultivated plots, and 15.2 and 29.8 for the 2,4-D-treated plots.

In late August, the cultivated corn was much better in all respects than either the 2,4-D-treated (fig. 2) or the flame-cultivated. Besides being darker green, the stalks were thicker and the ears larger and more numerous than on the other plots. The average increase of 40 bushels of corn per acre obtained on plots cultivated for the control of weeds as compared with those treated with 2,4-D is at variance with results of other investigators (1)[2]. A decrease of about 9 bushels per acre for the flamed corn in comparison with cultivated corn was obtained. It was noticed that after the flamed corn was cultivated, it became darker green.

TABLE 2

Field-moisture percentages of soils cropped to corn and treated with 2,4-D, cultivated, or flame-cultivated for control of weeds; of soil in adjacent areas† in bluegrass sod; and of soil in tractor turn-around areas*

DEPTH	2,4-D		CULTIVATED				FLAME-CULTIVATED				SOD‡	LALEYS§
	Organic + Mineral Fertilizer	Mineral Fertilizer	Organic + Mineral Fertilizer		Mineral Fertilizer		Organic + Mineral Fertilizer		Mineral Fertilizer		Mineral Fertilizer	
	Plot C	Plot A	Plot E		Plot B		Plot F		Plot D		Samples taken opposite plots A, B, C, D, E, and F	
	Row 2–3	Row 2–3	Row 2	Row 2–3 (W)¶	Row 2	Row 2–3 (W)¶	Row 2	Row 2–3 (W)¶	Row 2	Row 2–3 (W)¶		
inches												
0–2	17.6	17.0	16.2	15.8	13.7	14.8	17.4	16.7	16.3	15.5	23.0	16.5
4–6	16.0	17.2	16.9	15.6	14.8	17.4	16.3	16.2	17.0	15.8	14.5	16.0
6–8	16.3	15.3	15.7	14.2	14.5	14.9	15.1	16.4	15.2	15.1	13.5	17.3
12–14	18.7	18.2	17.5	18.6	19.3	18.0	17.9	18.8	19.7	19.8	11.8	20.0
Average....	17.2	16.9	16.6	16.1	15.6	16.3	16.7	17.0	17.1	16.6	15.7	17.4

* Average of five soil-core samples per treatment: 0–2-, 4–6-, 6–8-inch depths sampled October 27–29; 12–14-inch depths sampled November 12 and 15, 1948.

† 0–2-, 4–6-, 6–8-inch depths sampled October 27–29; 12–14-inch depth sampled November 9 and 15, 1948.

‡ Area in orchard adjacent to corn plots. Average of six samples.

§ Between corn plots, used for turn-around areas for tractor. Average of five samples.

¶ Tractor-wheel area.

This fact, together with the yield in comparison with that from the cultivated plots, indicates the importance of loosening hardened surface soil.

Soil structure. Figures 3 and 4 show that the various methods of weed control produced indirect effects on the porosity of the soil. The greatest differences were in the surface 2 inches. Comparison of the 0–2- and 4–6-inch depths also shows large differences.

The effect of cropping land for a number of years and of traveling over an area repeatedly by a tractor for one crop season is brought out strikingly by a comparison of the porosity and volume weights for the 0–2-inch depth in the alley and bluegrass sod areas: the bluegrass sod had 68 per cent higher macroporosity, 29 per cent higher total porosity, and 25 per cent less volume weight. Comparative values for the mineral fertilized nontraveled cultivated areas were 35, 9, and 7 per cent, respectively. Thus the porosity and volume-weight values for the cultivated plots were intermediate between the alley and sod values.

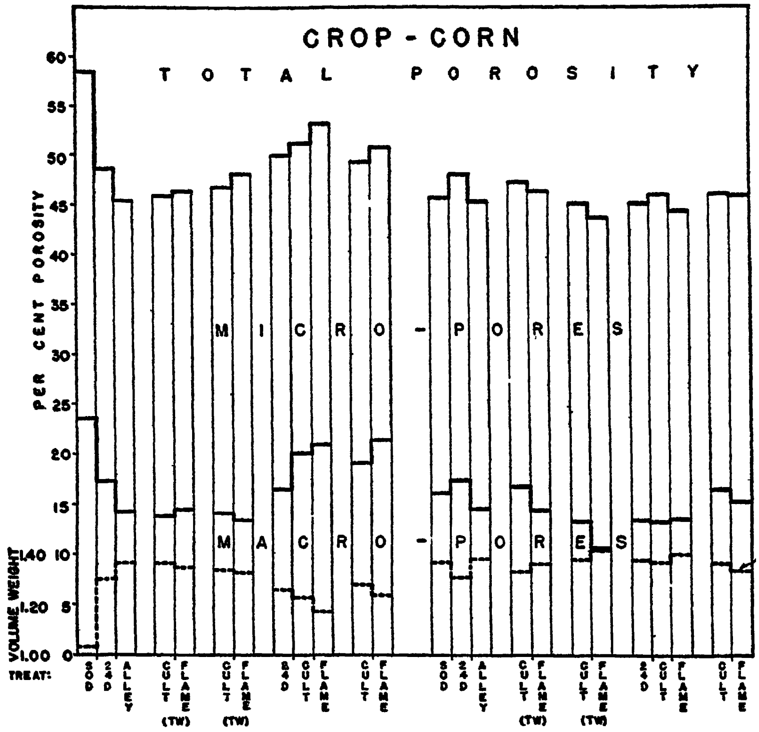

Fig. 3. Effects of Soil Treatments on Porosity and Volume Weights of 0–2- and 4–6-Inch Depths

Plots in continuous sod for 12 years compared with corn plots receiving 2,4-D only, flaming plus one cultivation, and cultivation treatments for control of weeds. The corn plots received mineral fertilizers only or mineral and organic (barnyard manure) fertilizers. Soil-core samples were taken in the sod, in areas traveled over by the rear tractor wheel (TW), in untraveled areas between hills of corn, and in a turn-around (noncultivated) area (alley) for the tractor at the ends of the plot.

This brings out the effect of cultivation in loosening the soil, provided no tractor wheel passes over the ground.

Comparisons for the three treatments between the 0–2- and 4–6-inch depths show the effect of bluegrass in maintaining a high porosity in the surface 2 inches of soil. Percentage decreases in macroporosity from the 0–2- to the 4–6 inch depths for the bluegrass sod, cultivated, and alley areas were 47, 15, and 3 per cent; for total porosity 28, 7, and 0; and for volume weight 25, 7, and 0 per cent, respectively. Differences in porosity and volume weight among the various treatments at the 4–6-inch and subsequent sampling depths were much less. These smaller differences suggest the importance of maintaining the surface in good tilth.

Soil physical differences (surface 2 inches) between areas traveled over by the rear tractor wheel and nontraveled areas between the rows (fig. 3) show that tractor weight and vibration effect compact the soil, even when a cultivator shovel follows the rear wheel. Porosity and volume-weight values for the alley and tractor-wheel areas were of the same magnitude.

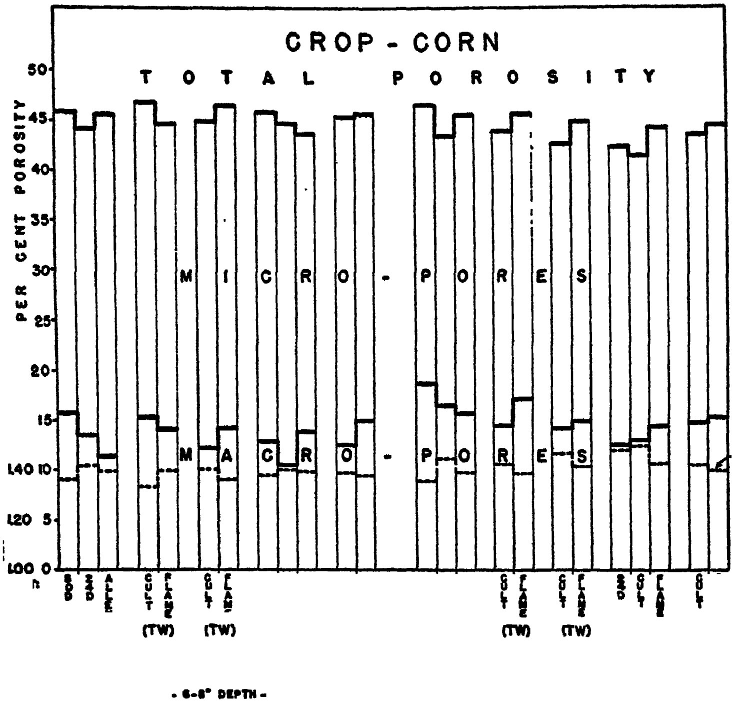

FIG. 4. EFFECT OF SOIL TREATMENTS ON POROSITY AND VOLUME WEIGHTS OF 6–8- AND 12–14-INCH DEPTHS OF PLOTS IN FIGURE 3

Figures 3 and 4 show that, in nearly every case, where there was an increase in volume weight, there was a corresponding decrease in macropores and total porosity and an increase in micropores.

For comparison, the 2,4-D mineral-fertilized plot (fig. 3) can be used as a standard. In this treatment, the soil was not disturbed after seedbed preparation. Apparently in the untraveled areas between the rows, for the surface 2 inches, cultivation increased total and macroporosity and decreased the micropores and volume weight. In the tractor-wheel areas, total and macroporosity decreased while the micropores and volume weight increased. This compaction pattern was not carried down to other depths to any great extent.

Comparison of the surface 2 inches of soil in the flamed corn plots and in the cultivated plots shows higher total porosity in the flamed plots, little difference in macropores and volume weight in the tractor wheel areas, and higher macroporosity and lower volume weight in the untraveled areas. This suggests that increased traveling over an area by a tractor decreases the total and macroporosity and increases the volume weight and microporosity in the surface soil.

An analysis of variance (11) for all depths in the corn plots showed that statistically the decrease in macropores in the area traveled by the rear tractor wheel in comparison with the nontraveled area (figs. 3 and 4) was significant at the 5 per cent level (4). When only the data for the 0–2-inch depth were compared statistically, the effect of compacting soil by going over it with a tractor in comparison to no tractor was highly significant at the 0.1 per cent level for the macropores, total porosity, and volume weight, and significant at the 0.5 per cent level for micropores.

TABLE 3

Field-moisture percentages of soils cropped to carrots and treated with oil spray or cultivated for control of weeds, of soil in adjacent areas† in bluegrass sod, and of soil in tractor turn-around alleys*

DEPTH	OIL SPRAY		CULTIVATED				SOD‡	ALLEYS§
	Organic + Mineral Fertilizer	Mineral Fertilizer	Organic + Mineral Fertilizer		Mineral Fertilizer		Mineral Fertilizer	
	Plot D	Plot B	Plot C		Plot A		Samples taken opposite plots A, B, C, and D	
	4–5	4–5	3–4	4–5 (W)¶	3–4	4–5 (W)¶		
inches								
0–2	15.3	15.7	15.4	14.4	14.9	14.9	15.9	13.8
4–6	14.9	13.9	14.7	12.9	14.9	14.5	11.6	14.9
6–8	14.3	13.9	16.9	13.5	15.3	14.4	12.7	14.6
12–14	14.9	14.0	16.0	15.0	16.4	17.7	12.6	16.7
Average..........	14.8	14.4	15.8	13.9	15.4	15.4	13.2	15.0

* Average of five soil-core samples per treatment: 0–2-, 4–6-, 6–8-inch depths sampled October 18–20; 12–14-inch depths sampled November 9 and 12, 1948.

† Average of five soil-core samples: 0–2-, 4–6-, 6–8-inch depths sampled October 21; 12–14-inch depth sampled November 12, 1948.

‡ Area in orchard adjacent to carrot plots. Average of five samples.

§ Between carrot plots, used for turn-around areas for tractor. Average of five samples.

¶ Tractor-wheel area.

There were no statistically significant soil physical differences between plots treated with mineral fertilizer and plots treated with organic plus mineral fertilizer. Since this experiment has been in effect only for 1 year, it was not expected that large differences of this kind would be evident. After a period of years, the manure-treated plots can be expected to have the better structure. Figure 3

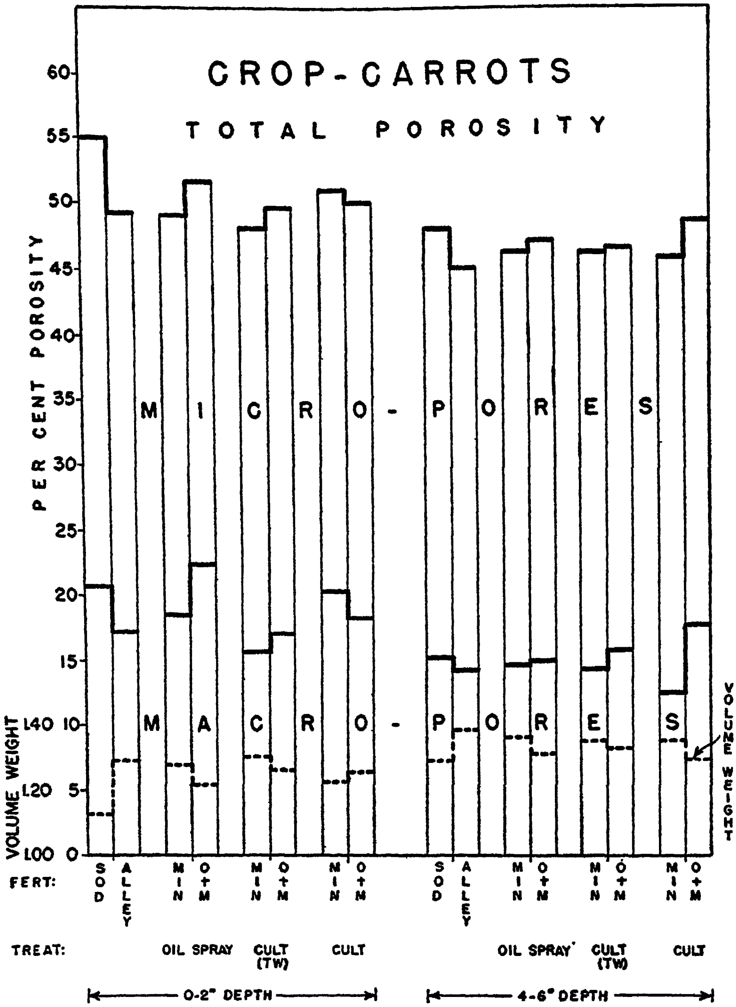

Fig. 5. Effects of Soil Treatments on Porosity and Volume Weights of 0-2- and 4-6-Inch Depths

Plots in continuous sod for 12 years compared with carrot plots receiving oil spray only and cultivation treatments for control of weeds. The carrot plots received mineral fertilizers only or mineral and organic (barnyard manure) fertilizers. Soil-core samples were taken in the sod, in areas traveled over by the rear tractor wheel (TW), in untraveled areas in the row, and in a turn-around (noncultivated) area (alley) for the tractor at the end of the plot.

does show, however, that addition of barnyard manure improved soil structure in the surface 2 inches in comparison to the plots to which none was added.

Carrots

Growth. The adverse weather conditions did not seem to affect the carrots so much as the corn. In the early part of the season, the cultivated carrots were more vigorous and somewhat larger in size than the uncultivated. By September, however, there was no noticeable difference in size and growth.

The differences in soil-moisture content (table 3) between treatments was not so great for carrots as for corn. The slightly higher moisture content in the surface 2 inches of the noncultivated oil-spray plots was probably not large enough to make any appreciable differences in yield of carrots.

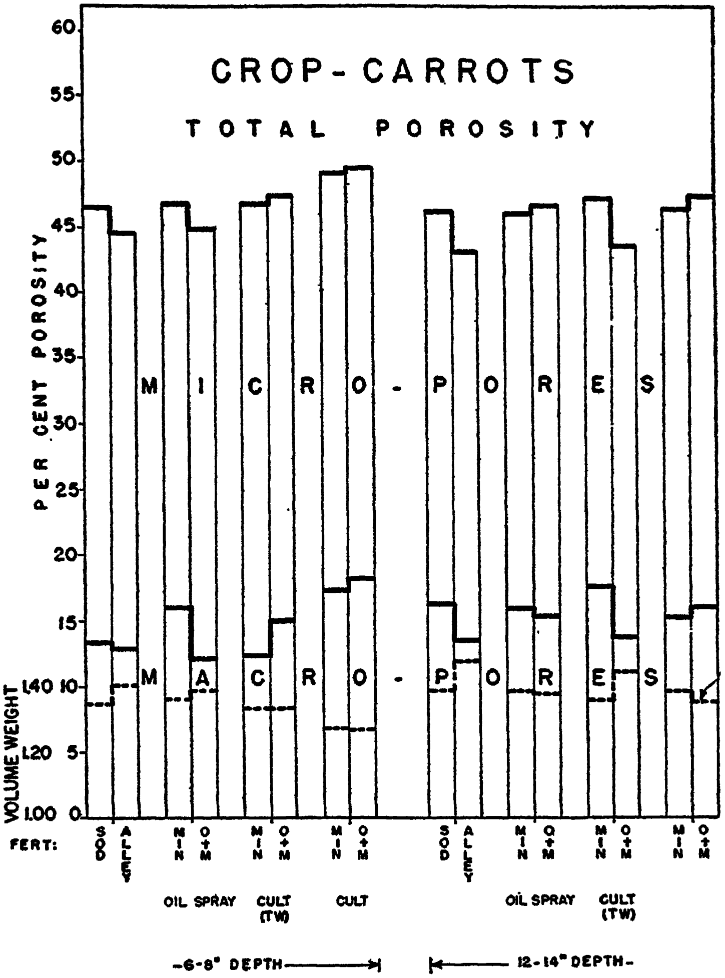

FIG. 6. EFFECT OF SOIL TREATMENTS ON POROSITY AND VOLUME WEIGHTS OF 6–8- AND 12–14-INCH DEPTHS OF PLOTS IN FIGURE 5

Packing of the ground by heavy rains did not seem to affect the yield of carrots so much as of corn. Yields were higher for plots heated with mineral fertilizer (927 bushels per acre under oil-spray and 996 bushels under cultivation) than for plots treated with barnyard manure and mineral fertilizer (849 bushels per acre under oil spray and 921 bushels under cultivation).

Soil structure. Figures 5 and 6 show that the treatments of carrot plots produced smaller soil physical differences than did the treatments of corn plots. The packing of the tractor wheel in the 0–2-inch depth decreased macroporosity and total porosity and increased microporosity and volume weight (fig. 5).

When all four sampling depths were considered statistically by the analyses of variance method, none of the physical soil data were found to be significant. When statistical comparisons were made on the effect of tractor wheels versus no-tractor wheels for only the 0–2-inch depth, however, the differences were found to be highly significant at the 1 per cent level for the macropores and significant at the 5 per cent level for volume weight, microporosity, and total porosity.

In the case of the effect of tractor wheels on organic versus mineral sources of fertilizer, the differences just missed being significant at the 5 per cent level for the macropores and volume weight.

DISCUSSION AND CONCLUSIONS

One year's results cannot be expected to show conclusively the effects of cultivation versus noncultivation on soil physical properties. The data indicate that cultivation is beneficial under certain conditions, such as abnormally high rainfall coupled with hard downpours of rain. These hard rains pack the soil, forming a crust on the ground surface. Breaking up this crust aerates the soil, providing oxygen for soil organisms so that nitrates can be produced for the plants. The fact that this kind of condition exists is shown by a comparison of the corn plants in figures 1 and 2.

For the soil studied, the greatest quantity of macropores was found in the 0–2-inch depth. If the quantity of these macropores is decreased, as in the tractor-wheel area, there is less opportunity for air and rainfall to enter the soil. Over a period of years, it is conceivable that the weight and vibrating effect of tractors decrease the macroporosity of soils. This would be especially true where tractors are run over the ground many times each crop season. For some soils this would mean less infiltration capacity and more runoff, producing more erosion. The increased use of tractors and heavy machinery in the last 25 years or so may be another cause of accelerated soil erosion.

Although quantitative data were not obtained for nitrate production for the various treatments of the corn plots, qualitative observations (figs. 1 and 2) strongly suggest that tight, crusted soil surfaces limit entry of air into the soil and reduce nitrate production. An average yield increase of 40 bushels of corn per acre when the surface crust was broken, as in the cultivated plots, in comparison with the 2,4-D plots, which were not disturbed after planting, also strongly suggests the importance of breaking the crust. The 9-bushel average decrease in yield per acre for the flamed corn, in which the soil crust was broken by a single cultivation, in comparison with cultivated corn indicates the importance of loosening hardened surface soil. Statistical calculations also bear out the importance of the surface layer in relation to plant growth.

Since moisture in the soil is depleted both by corn and by weeds, it would be expected that the 2,4-D plots (fig 2) would be lowest in moisture. This was not true (table 2). More moisture evidently was taken from the cultivated plots (weed-free) by the vigorously growing corn plants than from the flame or 2,4-D plots (weeds present). Cultivation may slso have reduced the soil moisture content.

Although only one moisture sampling was made, it is believed that additional samplings would have fallen in the same pattern. Rainfall and temperature data in table 1 show that droughty conditions existed during September and October. Little rainfall was lost by runoff, and since the plots were randomized, runoff differences due to treatments and plot location on the 3 to 5 per cent slope would be minimized as well as averaged for the various treatments.

Under the conditions of this experiment, soil moisture apparently was not the only factor limiting growth of corn plants. Other factors such as tilth appear to be just as important. Cultivation improved soil tilth as measured by an increase in total and macroporosity and a decrease in microporosity and volume weight in the surface 2 inches (untraveled area) in comparison with the noncultivated 2,4-D plots (fig 3). This improved soil tilth may have been just as important a factor in plant growth as was soil moisture. Poor soil structure as measured in the 2,4-D plots in comparison with the cultivated ones may have overshadowed the higher soil moisture in the 2,4-D plots. Perhaps good soil tilth is just as important a factor in crop growth as is the control of weeds to eliminate uptake of soil moisture and nutrients used otherwise by crop plants.

When growth and yield of carrots and corn are considered, the carrot taproot system evidently can live better in adverse soil conditions than can corn with its fibrous root system.

It is believed that part of the soil structure differences obtained between the corn and carrot plot tractor-wheel areas can be ascribed to the differences in weights of the tractors used.[6] In each case the rear wheel traveled over the wheel-track area twice—once going down the row and again on the return trip when the adjacent rows were cultivated. From the data obtained (figs. 3–6), it appears that light-weight tractors are to be preferred to the heavier models for least soil compaction.

Large significant differences in soil physical properties for the organic plus mineral fertilizer and mineral fertilizer alone were not obtained in 1 year's study. It is believed, however, that over a period of years, the soil treated with organic fertilizer would become less compact than the mineral-fertilized soil. In this connection, Parker and Jenny (10) have reported that incorporation of organic matter as manure or cover crop improved soil structure.

SUMMARY

A report of 1 year's study on the effect of using 2,4-D and flaming and their indirect effect on soil structure versus killing weeds by the usual cultivation methods is reported. Corn and carrots were the crops used. On the basis of the data obtained, the experiment has been revised and will be continued for a number of years.

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[6] Weight of corn tractor with cultivator but without operator, 4020 pounds; weight of carrot tractor with cultivator but without operator, 2910 pounds.

Measurements of volume-weight and pore-space relationship (total, macroporosity, and microporosity) were made on core samples taken at 0–2-, 4–6-, 6–8,- and 12–14-inch depths in the area traveled over by the rear tractor wheel, in untraveled areas in the hills between rows, and in the turn-around areas used during cultivation. Samples were taken from an adjacent bluegrass sod area for comparison.

Heavy rains early in the season and subsequent hot dry weather resulted in soil crusting. It is believed that this crust prevented free entrance of air into the soil, resulting in reduced soil nitrification. The corn plants showed definite nitrogen starvation, although the carrots were not visible affected.

An average increase of 40 bushels of corn per acre was obtained for plots cultivated for the control of weeds as compared with those treated with 2,4-D applied at the rate of 1½ pounds of sodium salt spray per acre.

A devrease of about 9 bushels of corn per acre for the flamed corn in comparison with cultivated corn was obtained. This small difference in yield may have been due to breaking of the soil crust by a single cultivation.

It was found that in one season the soil in the tractor-wheel area in cultivated corn plots was packed more than in nontractor-wheel areas.

In the 0–2-inch depth, the bluegrass sod had 68 per cent higher macroporosity, 29 per cent higher total porosity, and 25 per cent lower volume weight than the alley turn-around areas; corresponding values for the cultivated nontractor-wheel area were 35, 9, and 7 per cent respectively. This points out the effect of cultivation in loosening the soil, provided no tractor wheel passes over the ground and it is not cultivated when the soil is wet.

Percentage decreases in macroporosity from the 0–2- to the 4–6-inch depths for the bluegrass sod, cultivated nontractor wheel, and alley areas obtained were 47, 15, and 3 per cent; for total porosity 28, 7, and 0; and for volume weight 25, 7, and 0 per cent, respectively. Differences in porosity and volume weight among the various treatments at lower depths were small.

Soil structure differences in the 0–2-inch depth alone were found to be more significant statistically than when all four sampling depths (0–2-, 4–6-, 6–8-, 12–14-inch) were considered together.

The 0–2-inch depth showed less packing effect in the tractor-wheel area in the carrot than in the corn plots. Also, higher statistically significant values for soil physical data were obtained for corn than for carrots. This was probably due to differences in weights of tractors used.

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ALFALFA FERTILITY INVESTIGATIONS IN SOUTH CAROLINA

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A successful livestock program would contribute much toward establishing a stable diversified agriculture in the South. Such a program, however, demands a feed supply produced on the farm at relatively low cost. Since the fully owned farm units in South Carolina are small, averaging 101.1 acres, of which only 41.4 acres are classed as cropland (15), production of sufficient feed to support a livestock enterprise is difficult, especially with the common forage crops and practices.

Annual lespedeza (3) has gained wide popularity as a forage legume in the Southeastern States, because it persists on acid soils of low fertility. It is, however, a shallow-rooted legume which normally produces only one cutting of hay, rarely exceeding 1.5 tons a year. Lespedeza hay usually contains less protein, phosphorus, calcium, and magnesium than alfalfa. Although *Lespedeza sericea* is a deep-rooted, drought-resistant perennial legume, its top growth is killed by frost, and the quality and yield of hay are usually poor. Alfalfa, in contrast, is more palatable than sericea, and is a deep-rooted, drought-resistant perennial legume which grows about 10 months of the year, thus utilizing the long growing season of the South. It produces four or five cuttings each year, and an acre often yields 3 or more tons of hay with high protein and mineral content. If this production can be assured, alfalfa offers many advantages to farmers, especially to those with small acreages.

During the period 1940–1944, the alfalfa acreage in the Southeast increased from 68,482 to 80,721[2] acres (16) despite the difficulties in obtaining potassium fertilizer materials. Although during this period alfalfa decreased from 1742 to 842 acres in South Carolina, alfalfa seed purchases in 1946 and 1947 indicate that many farmers in this state are attempting to grow the crop. The increasing use of alfalfa has been made possible by investigations of fertility and management practices, conducted during the last few years. Knowledge of lime requirement (1, 6, 13), use of boron (4), seeding methods, effective inoculation, adapted varieties, and liberal use of phosphorus and potassium (13) are all essential tc successful alfalfa production. Cooper (2) reported that approximately 40 pe cent of more than 2,000,000 soil samples in South Carolina had a pH value o 5.5 or less and were classified as strongly to extremely acid.

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[2] States included 1939–1944: Virginia, North Carolina, South Carolina, Georgia, an Alabama.

Alfalfa produces maximum hay yields when grown on deep, well-drained soils well supplied with nutrients. Lucas *et al.* (5) and Snider (10) reported that a 3-ton crop of alfalfa may remove 25 to 40 pounds P_2O_5 and 90 to 120 pounds K_2O. In addition to phosphorus and potassium, large amounts of sulfur, calcium, and magnesium and small amounts of boron are required for normal growth. Relatively small amounts of these elements are present in soils of the Piedmont and Coastal Plain regions, and they must be supplied before alfalfa can be grown successfully. In farm operations, fertilizers are generally applied to the surface and then worked into the top 3 or 4 inches of soil. Recent investigations, however, have cast doubt on the efficiency of surface fertilizer applications for deep-rooted legumes. Midgley[3] reported that on an acid soil, fertilizer mixed with manure produced greater yields of alfalfa when plowed under than when harrowed into the surface; likewise, 400 to 1,000 pounds of 3-12-6 produced greater yields when plowed under than when applied in the surface. Banding on the bottom of the plow furrow produced greater yields than broadcasting and plowing the material under. Pohlman (8) showed that liming by layers at different depths in an acid soil stimulated fibrous root and nodule development in the lime zone irrespective of whether it occurred at 8 to 16 inches or 16 to 24 inches. Toevs and Baker (11) reported that the presence of a plentiful supply of available phosphorus was directly related to alfalfa root development, which increased the feeding area of the plant. Stimulation of fibrous root and nodule development of alfalfa by placing lime and fertilizer in the cooler lower layers of the soil offers promise of increased drought resistance and increased efficiency of nitrogen fixation. Work cited by Wilson (14) indicates that symbiotic nitrogen fixation is decreased when soil temperatures exceed 70° F. Temperatures well above this point occur in the surface 6 inches of soil in the Southeastern States during summer. Unpublished data by the authors indicate that summer soil temperatures range from 6° to 13° F. lower and moisture content is higher at a depth of 12 than of 3 inches.

Supplying the nutrient elements required to produce high yields of alfalfa over a period of years presents several problems. Applying all of the nutrients at planting time greatly increases the initial cost and may be inefficient because of fixation or erosion losses. Toevs and Baker (11) reported that much greater yields were obtained by applying phosphorus to a new seeding of alfalfa than to an old stand. Willard *et al.* (13) reported important yield increases produced by applying phosphorus and potassium at time of seeding, but also found that top-dressing alfalfa with phosphorus and potash after the first cutting increased both yield and longevity of stand. Bear and Prince (1) stated that the soil on which alfalfa is to be grown should be well fortified with calcium and magnesium in preparation for seeding, but that the potassium applications should be governed by the specific annual needs of the plant, a suitable application being made at seeding time and additional quantities being supplied each year.

The objectives of the present investigation were to study the effects of initial and maintenance applications of fertilizer, and depths of placement of lime and phosphate, on establishing stands of alfalfa; on yield and composition of hay; and on longevity of stand, including resistance to cold, drought, and disease.

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[3] Private communication.

PROCEDURE

A field experiment was established with Kansas Common alfalfa on well-drained Cecil clay loam in the fall of 1946. This land had received limited amounts of fertilizer and had been in cotton for 10 years prior to 1942 and was in weeds from 1942 to 1946. The soil was sampled before lime and fertilizer were applied and was analyzed (7) as shown in table 1. The alfalfa seed was produced in Oklahoma and was inoculated with material supplied by the soil microbiology laboratory at Beltsville.

TABLE 1

Exchangeable cations, acidity, organic matter, and phosphorus content of untreated soil

SAMPLE DEPTH	pH	ORGANIC MATTER	PHOSPHORUS		EXCHANGEABLE CATIONS				TOTAL BASE-EXCHANGE CAPACITY
			Total	Troug	K	Ca	Mg	H	
inches		*per cent*	*lb./A.*	*lb./A.*	*me.**	*me.**	*me.**	*me.**	*me.**
0- 8	5.7	1.3	540	<25	0.39	1.3	0.24	1.8	3.80
8-16	5.0	0.6	445	<25	0.24	1.1	0.24	2.0	3.66

* Per 100 gm.

Plot layout

The experimental design was a latin square for main treatments, consisting of three plow-sole fertilizer treatments with three replications. The subplots were a four by four factorial consisting of four initial surface treatments before planting, with four maintenance treatments applied to the surface the first year, after the first hay cutting.

Main blocks (60 by 80 feet) were treated as follows:

1. Nothing on plow sole.
2. 1,000 pounds dolomite, bands 12 inches apart and 8 inches deep.
3. 1,000 pounds dolomite plus 180 pounds P_2O_5, bands 12 inches apart and 8 inches deep.

Subblocks (20 by 60 feet), randomized in the main blocks, were treated as follows before planting:

1. Basic treatment (20 pounds borax; 400 pounds 4-10-6 drilled 3 inches deep in rows 7 inches apart; 5,000 pounds dolomite disked into surface 4 inches of soil).
2. Basic treatment plus 180 pounds P_2O_5 in bands 3 inches deep, 7 inches apart.
3. Basic treatment plus 200 pounds K_2O in bands 3 inches deep, 7 inches apart.
4. Basic treatment plus the additions used in 2 and 3.

Plots (15 by 20 feet), randomized in the subblocks, were treated as follows after the first cutting:

1. No additions.
2. 60 pounds K_2O.
3. 120 pounds K_2O.
4. 120 pounds K_2O plus 180 pounds P_2O_5.

Superphosphate (18 per cent P_2O_5), muriate of potash (50 per cent K_2O), and dolomite were used as the source of potassium, phosphorus, and lime, and all applications are reported in pounds per acre.

Method of applying fertilizer

The dolomite and superphosphate treatments of the main blocks were made with an International Harvester plow-sole distributor No. 46 mounted on a single disc plow. Surface applications of lime and fertilizer to the subblocks were made with the fertilizer distributor of a 9-foot grain drill. This drill was used also in applying the maintenance treatment of phosphorus in bands 7 inches apart and 2.5 inches deep on the established stand after the first cutting. The maintenance treatment of potash was applied on the surface with a 5-foot Gandy spreader after the first cutting.

Harvesting

An area 9 by 14 feet was harvested from the 15 by 20-foot plots. The alfalfa was cut, at one-fourth bloom, with a power scythe mower. Immediately before harvesting of each plot, a subsample composed of five stems from each of ten locations (50 stem samples per plot) was collected for moisture and chemical analysis. Samples were dried for 48 hours in an oven at 95°C. The green alfalfa was raked and weighed immediately after mowing. Hay yields were calculated at 15 per cent moisture.

Chemical analysis

Oven-dried plant material was ground in a Wiley mill. Samples were ashed by wet digestion with nitric acid initially, and finally with 60 per cent perchloric acid. The residue was transferred, made up to volume, and filtered. Phosphorus was determined by a modification of Sherman's method (9). The cations were determined with a Perkin-Elmer Flame Photometer, Model 52A.

RESULTS AND DISCUSSION

The data presented in table 4 show that a yield of 14,510 pounds or an increase of 5,130 pounds of alfalfa hay per acre was produced in seven cuttings in 2 years by the combination of highest rates of phosphorus and potassium (average of plots receiving 220 pounds P_2O_5 banded 3 inches deep plus 180 pounds P_2O_5 in bands 8 inches deep with 224 pounds of K_2O initially and 0, 60, or 120 pounds of K_2O per acre after the first cutting in 1947) over that produced by the basic rate of phosphorus and potassium. The increase in phosphorus content of the hay in the first and second cuttings and the yield response to superphosphate indicated that phosphorus was the main factor limiting growth

TABLE 2

Effect of phosphorus rate and placement on yield of alfalfa grown on Cecil clay loam

PHOSPHORUS TREATMENTS*		YIELD OF ALFALFA HAY, 1947, BY CUTTINGS		
P_2O_5/acre	Placement	First	Second	Total
lb.		*lb./A.*	*lb./A*	*lb./A.*
40	Band 7 inches apart—3 inches deep	1186	1480	2666
40 + 180	Band 7 inches apart—3 inches deep	1732	1897	3629
40 + 180	Band 7 inches apart—3 inches deep Band 12 inches apart—8 inches deep	1740	2064	3804
40 + 180 + 180	Band 7 inches apart—3 inches deep Band 12 inches apart—8 inches deep	2098	2242	4335

* Plots received 224 pounds K_2O before planting. Significant difference at 5 per cent level: first cutting, 563 pounds/acre; second, 673 pounds/acre. Weather was extremely dry during growth of second cutting.

TABLE 3

Effect of phosphorus rate, placement, and time of application on absorption of phosphorus and yield of alfalfa grown on Cecil clay loam, 1947

One replicate

TREATMENT* NUMBER	P_2O_5 APPLIED BEFORE PLANTING		FIRST CUTTING			P_2O_5 APPLIED AFTER FIRST CUTTING	SECOND CUTTING			TOTAL	
	Surface	Subsoil	Hay Yield	P_2O_5 Content	P_2O_5 Removal		Hay yield	P_2O_5 Content	P_2O_5 Removal	Hay yield	P_2O_5 Removal
	lb./A.	*lb./A.*	*lb./A.*	*per cent*	*lb./A.*	*lb./A.*	*lb./A.*	*per cent*	*lb./A.*	*lb./A.*	*lb./A.*
1	40	0	1409	0.417	5.86	0	1759	0.582	10.23	3165	16.09
2	220	0	1581	0.460	7.37	0	1480	0.568	8.41	3061	15.87
3	220	0	1632	0.442	7.21	180	1933	0.690	12.34	3565	19.55
4	40	0	1760	0.416	7.32	180	2226	0.674	14.01	3986	21.33
5	40	180	2088	0.518	10.82	0	2025	0.644	13.04	4113	23.86
6	40	180	1823	0.513	9.35	180	2253	0.704	15.86	4076	25.21
7	220	180	2441	0.598	14.60	0	2574	0.644	16.58	5015	31.18
8	220	180	2361	0.566	13.36	180	2802	0.674	18.99	5163	32.25

* Detailed treatments were as follows:

1. Basic (400 pounds 4-10-6 band 7 inches apart, 3 inches deep before planting)
2. Basic + 180 pounds P_2O_5 band 7 inches apart, 3 inches deep before planting
3. No. 2 + delayed 180 pounds P_2O_5 band 7 inches apart, 2½ inches deep
4. Basic + delayed 180 pounds P_2O_5 band 7 inches apart, 2½ inches deep
5. Basic + 180 pounds P_2O_5 band 12 inches apart, 8 inches deep before planting
6. No. 5 + delayed 180 pounds P_2O_5 band 7 inches apart, 2½ inches deep
7. No. 5 + 180 pounds P_2O_5 band 7 inches apart, 3 inches deep before planting
8. No. 7 + delayed 180 pounds P_2O_5 band 7 inches apart, 2½ inches deep

of alfalfa during the first few months on this soil (tables 2 and 3). Field observations indicated that banding of phosphorus was highly important.

TABLE 4

Effect of rate and placement of fertilizer on yield of alfalfa

Fertilizer treatments and yields in pounds per acre

INITIAL FERTILIZER APPLICATIONS			YIELD OF HAY, SEVEN CUTTINGS,† WITH MAINTENANCE FERTILIZER APPLIED AFTER FIRST CUTTING					TREATMENT REPLICATIONS‡
Surface		Plow sole§	K_2O 0	K_2O 60	K_2O 120	Av. K_2O (0, 60, 120)	P_2O_5 K_2O 180 120	
P_2O_5	K_2O	P_2O_5						
0	0	0	9,660	9,130	9,340	9,380	11,020	6
0	0	180	12,400	12,120	12,340	12,290	12,140	3
180	0	0	10,820	11,040	11,170	11,010	11,130	6
180	0	180	10,730	12,990	12,170	11,970	12,520	3
0	200	0	10,200	10,450	10,560	10,410	10,950	6
0	200	180	12,840	11,930	12,670	12,480	12,370	3
180	200	0	10,880	11,400	11,340	11,200	12,050	6
180	200	180	14,100	14,070	13,930	14,030	14,510	3

* Basic fertilizer treatment applied to all plots as follows: 5000 pounds dolomite disked into surface 4 inches of soil; 20 pounds borax; 400 pounds 4-10-6 drilled 3 inches deep, rows 7 inches apart.

† Formulas and data for use in obtaining standard errors for various treatment comparisons:

TREATMENT COMPARISONS**	STANDARD ERROR††
$(a_1b_1)—(a_0b_1)$	$\sqrt{2\{(B - 1)E_b + E_a\}/rB}$
$(a_1b_1)—(a_1b_0)$	$\sqrt{2\ E_b/r}$
$(a_1c_1)—(a_0c_1)$	$\sqrt{2\{r - 1)E_c + E_a\}/r\gamma}$
$(a_1c_1)—(a_1c_0)$	$\sqrt{2\ E_c/r}$
$(b_1c_1)—(b_0c_1)$	$\sqrt{2\{(B - 1)E_d + E_b\}/r\alpha B}$
$(b_1c_1)—(b_1c_0)$	$\sqrt{2\{(\gamma - 1)E_d + E_c\}/r\alpha\gamma}$

** The symbols $a_0 - a_1$ represent the difference between *A* means (plow-sole fertilizer treatments); $b_0 - b_1$, the difference between *B* means (initial surface fertilizer treatments); and $c_0 - c_1$, the difference between *C* means (maintenance fertilizer treatments).

†† Error mean square E_a = 623,597 (2 degrees of freedom), α = number of A treatments
E_b = 3,106,259 (18 degrees of freedom), β = number of B treatments
E_c = 410,725 (18 degrees of freedom), γ = number of C treatments
E_d = 629,152 (54 degrees of freedom), mean square for B × C and A × B × C interactions.

Acknowledgment is due J. A. Rigney, North Carolina Agricultural Experiment Station, for the formulas in this table.

‡ There are 18 and 9 replications respectively represented in the column showing average maintenance K_2O corresponding to the 6 and 3 replicates for the other treatments.

§ Treatments of nothing, and dolomite on the plow sole were pooled and only the averages are shown since there was no response to plow-sole dolomite.

In the first year 1,000 pounds of superphosphate in bands 12 inches apart and 8 inches deep (plow-sole placement) produced about the same yield of hay in each of two cuttings as this amount of superphosphate in bands 7 inches apart and 3 inches deep (table 2). The percentage phosphorus in the hay was higher in each of two cuttings (table 3, treatments 2 and 5), and 50 per cent more phosphorus was removed from the plots receiving the 8-inch than from those receiving the 3-inch depth placement. This indicated that on this soil, first-year alfalfa plants effectively absorbed phosphorus placed 8 inches deep. The 40 pounds of P_2O_5 applied in bands in the surface 3 inches of this soil appeared to be sufficient to stimulate early growth of alfalfa.

A large yield response was produced by rate and placement of phosphorus in the total of seven cuttings, two in 1947 and five in 1948 (table 4). These yields are the averages for the plots receiving 224 pounds K_2O initially plus 0, 60, or 120 pounds K_2O after the first cutting. The addition of 180 pounds P_2O_5 to the basic 40-pound P_2O_5 application produced 11,200 pounds of hay when banded 3 inches deep and 12,480 pounds when banded 8 inches deep—yield increases of 790 and 2,070 pounds for the 3- and 8-inch depths of phosphorus placement, respectively. By adding the increase produced by the 3- and 8-inch placements, an increase of 2,860 pounds would be expected when these two treatments were combined. However, the combination of 180 pounds P_2O_5 at 3-inch and 180 pounds P_2O_5 at 8-inch depths produced 14,030 pounds of hay, or an increase of 3,620 pounds. This increase of 760 pounds was produced by the interaction of shallow and deep placement of phosphorus. This greater yield response to deep placement of phosphorus may be the result of an increase in root development in the deeper soil horizons, allowing the plant greater access to other nutrients and to moisture during the frequent summer droughts. Alfalfa plants with 8-inch depth of phosphorus placement were observed to wilt less during hot, dry weather than those with 3-inch placement.

Maintenance phosphorus

One phase of this investigation involved the application of superphosphate after the first cutting as a maintenance treatment. A delayed or maintenance application of 180 pounds P_2O_5 was made after the first cutting in 1947 to plots which had received only 40 pounds P_2O_5 initially (table 4). The yields of the first cutting of hay were included in the total for seven cuttings, since an objective was to compare the over-all yield effects of 180 pounds P_2O_5 as an initial and as a maintenance treatment. The increases in hay yields for the total of seven cuttings were 1,640 pounds for the maintenance phosphorus applied after the first cutting, and 1,630 pounds for plots which had received an equal amount of phosphorus at the 3-inch depth initially. Hay produced in the cutting immediately following the application of maintenance phosphorus (table 3, treatments 4 and 2) contained more phosphorus than hay from plots which had received an equal amount of phosphorus initially. Thus composition and yield increases indicated that on this soil phosphorus applied at a depth of 2.5 inches with a grain drill fertilizer distributor after the first cutting was effective.

The 180-pound application of maintenance phosphorus produced significant yield increases on plots that had received 40 plus 180 pounds P_2O_5 initially at the 344 pound K_2O level, but not at the 144 pound K_2O level (table 4). The combination of the maintenance and 180 pounds P_2O_5 at the 8-inch depth did not produce significant yield increases. This suggested that either the deeper placement supplied the phosphorus requirements or that deeper placement stimulated root development in a deeper horizon of the soil so that these plants with deeper phosphorus placement could not effectively absorb the maintenance phosphorus that was placed near the surface.

Plow-sole placement of dolomite

There was no yield increase resulting from the plow-sole placement of dolomite alone over that produced by 5,000 pounds of dolomite disked into the surface 4 inches of soil. The mean yield of all treatments with nothing on the plow-sole was 10,690; with 1,000 pounds of dolomite on plow-sole, 10,800; and with 1,000 pounds of dolomite plus 1,000 pounds of superphosphate, 12,740 pounds of hay per acre. A significant increase resulted from the plow-sole placement of the superphosphate and dolomite together.

Effect of potassium fertilization

Yield increases produced by potassium were significant at the higher phosphorus levels. There was no indication of a response to the maintenance applications of K_2O over the basic rate of 24 pounds of K_2O per acre at the 40- or 220-pound initial rate of P_2O_5 (table 4). At the 400-pound initial rate of P_2O_5 however, significant increases were obtained by the initial and maintenance application of 200 and 120 pounds of K_2O respectively. Thus higher yields and more efficient use of potassium and phosphorus fertilizer applications can be realized only if neither element is allowed to become a limiting factor.

Chemical composition of dry alfalfa hay

High protein and mineral content of alfalfa or other legume hay is important in balancing the ration of livestock, especially dairy cows. For example, grain is low in calcium, and high-quality legume hay is depended upon to balance this deficiency. It has been reported (12) that if feed for fattening beef cattle contained less than 0.15 per cent phosphorus, the cattle developed definite phosphorus-deficient symptoms. A ration with higher phosphorus content would be required for dairy cows than for fattening beef cattle.

The yields and composition of the first and second cuttings in 1947 and the first cutting in 1948 are recorded in table 5. Placement of 180 pounds P_2O_5 at the 3-inch depth, in addition to the 40-pound P_2O_5 basic treatment, increased the content of phosphorus in the first cutting of hay in 1947 from 0.182 (near critical level) to 0.219 per cent (table 5, treatments 1B *vs.* 2B). Placing the 180 pounds P_2O_5 at the 8-inch depth on the plow-sole increased the phosphorus from 0.182 to 0.237 per cent (table 5, treatments 1B *vs.* 1A). The combination of 180 pounds P_2O_5 at 3-inch and 180 pounds P_2O_5 at 8-inch depths increased the phosphorus content from 0.182 to 0.253 per cent. The percentage of calcium and magnesium in the hay remained high, even with the greatest yield increases.

The marked increase in the percentage of phosphorus and sodium in the first cutting in 1948 as compared to the two 1947 cuttings is believed to have resulted from (*a*) allowing a late fall cutting in 1947 to remain on the land, thereby releasing available phosphorus and sodium to the first cutting in 1948, and (*b*) increased root development and storage during the fall of 1947 and spring of 1948. Although the percentage of phosphorus of this first cutting in 1948 was increased by higher phosphorus applications, the high over-all content of phosphorus offers one explanation for the lack of yield differences for rates of phosphorus in this cutting. Subsequent cuttings showed excellent response to phosphorus treatments.

TABLE 5

Yield and chemical composition of alfalfa hay grown on Cecil clay loam 1947–48

One replicate

TREATMENT*		HAY YIELD	COMPOSITION					TOTAL CATIONS
Block	Sub-block		P	K	Na	Ca	Mg	
		lb./A.	%	%	%	%	%	*m.e.*†
First cutting 1947								
A. Super-phosphate on plow-sole	1	2109	0.237	2.25	0.0181	1.68	0.390	174.2
	2	2135	0.253	1.94	0.0181	1.72	0.413	171.3
	3	1928	0.237	2.53	0.0175	1.55	0.391	176.0
	4	2459	0.248	2.48	0.0150	1.48	0.400	171.9
First cutting 1947								
B. No super-phosphate on plow-sole	1	1391	0.182	2.04	0.0207	1.58	0.468	170.4
	2	1564	0.219	2.00	0.0307	1.72	0.515	181.5
	3	1500	0.188	2.49	0.0151	1.43	0.380	167.9
	4	1829	0.207	2.30	0.0229	1.53	0.390	169.3
Second cutting 1947								
C. No super-phosphate on plow-sole	1	1347	0.172	2.03	0.0282	1.73	0.483	180.1
	2	1648	0.214	2.00	0.0385	1.80	0.526	186.7
	3	1477	0.182	2.38	0.0161	1.63	0.394	176.3
	4	1826	0.209	2.22	0.0232	1.40	0.388	160.3
First cutting 1948								
D. No super-phosphate on plow-sole	1	1737	0.326	1.87	0.0378	1.28	0.443	150.6
	2	1886	0.389	1.88	0.0478	1.32	0.501	158.0
	3	1795	0.339	2.28	0.0182	1.21	0.390	153.4
	4	1683	0.386	2.09	0.0405	1.21	0.430	151.8

* 1. Basic: 400 pounds 4-10-6, 5,000 pounds dolomite, 20 pounds borax
2. Basic + 1,000 pounds superphosphate (18 per cent P_2O_5)
3. Basic + 400 pounds KCl (50 per cent K_2O)
4. Basic + 1,000 pounds superphosphate + 400 pounds KCl

† Per 100 gm. of dry plant material.

The percentages of potassium, sodium, calcium, and magnesium in the hay and the total cation content expressed as milliequivalents per 100 gm. of plant material are presented in table 5. There was a tendency for the sum of the cations to be a constant value irrespective of treatment or cutting in 1947. All treatments yielded a lower sum of cations in the first cutting in 1948 than in either the first or second cutting of 1947. The potassium content was slightly lower and there was a sharp decrease in calcium content in the first cutting of hay in 1948 as compared to 1947. High rates of potassium with low phosphorus increased the potassium but produced a corresponding decrease in the calcium, magnesium, and sodium. This cation relationship has been reported by numerous investigators (1, 5).

SUMMARY

A satisfactory stand of alfalfa was established on Cecil clay loam low in fertility and organic matter by applying a basic treatment of 400 pounds of 4-10-6 fertilizer, 5,000 pounds dolomitic limestone and 20 pounds borax per acre. The yield and the phosphorus content of hay produced with this basic treatment were lower than those of hay produced with higher applications of phosphorus and potash.

Initially, available phosphorus was the major factor limiting plant growth.

Addition of 180 pounds of P_2O_5 to the basic phosphate application produced 11,200 pounds of hay when the phosphate was banded 3 inches deep and 12,480 pounds when banded 8 inches deep—yield increases of 790 and 2,070 pounds respectively in seven cuttings.

The combination of 180 pounds P_2O_5 banded 8 inches deep with 180 pounds P_2O_5 banded 3 inches deep (in addition to the basic phosphate application) produced 14,030 pounds of hay, or an increase of 3,620 pounds in seven cuttings.

Field observations indicated that banding of phosphorus was highly important.

During hot dry weather, plants with phosphorus banded at the 8-inch depth wilted less than those with phosphorus at 3-inch depths.

High rates of potash as well as phosphorus were required for maximum yields. The combination of highest rates of P and K produced 14,510 pounds of hay per acre, or an increase of 5,130 pounds in seven cuttings in 2 years.

The phosphorus content of the hay was increased and calcium and magnesium were maintained at a high level with the combination of highest rates of P and K.

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CHEMICAL COMPOSITION OF CERTAIN CALCIFUGOUS AND CALCICOLOUS PLANTS[1]

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It is now well known that some plants grow only within a rather narrow range of soil pH, while others grow well within wider ranges. Inasmuch as naturally acid soils are generally deficient in calcium, certain species which nearly always occur on acid soils are referred to as "calcifuges" or "calcifugous plants." On the other hand, some plants appear to be intolerant of acid soil conditions but grow favorably on neutral or alkaline soils; such species are termed "calcicoles" or "calcicolous plants" (3).

Opinions differ as to why certain species can thrive only on soils within a certain pH range. One view put forward by Hartwell and Pember (21) is that in very acid soils, certain quantities of active aluminum are present which are held to be toxic to calcicolous plants. Matson and Hester (39) have cautioned those who would simplify the problem by attributing the injurious action of acid soil to soluble aluminum. According to them, "... as far as relating aluminum toxicity to aluminum solubility is concerned, the relationship is complicated by the solubility and toxic effects of manganese and possibly other elements." Kirsanov (32) has suggested that "mobile" iron in acid soils is more harmful than "mobile" aluminum. Some investigators (2, 3), however, believe that the injurious effect of acid soil conditions on calcicolous plants is due to the calcium shortage usually associated with such conditions. On the other hand, Russell (47) referred to Salisbury's suggestion that calcifugous plants have a special need for potassium, which they might have some difficulty in obtaining on calcium-saturated soils. Small (51) has suggested that calcifugous plants have a dominant organic-acid metabolism, whereas calcicolous plants have dominant inorganic-acid, mainly phosphate and bicarbonate, metabolism.

The chief purpose of this investigation was to determine the chemical characteristics of certain calcifuges, calcicoles, and plants indifferent to soil pH in the natural environment. Special attention was given to the aluminum, iron, manganese, phosphorus, calcium, and potassium content of these plants. It was also expected from this examination to determine whether there may be a possible explanation of why plants of certain species thrive only on soils with a restricted range of pH.

In addition to the main purpose, this study had a threefold objective: first, to study the uptake of aluminum, iron, manganese, phosphorus, calcium, and potassium by the same species growing on different soils, from which it could be determined whether any relationship exists between the chemical composition of plants and the soil pH; second, to investigate the specific absorption of the six elements by plants of different species which grew side by side on the same natural soil; and third, to observe the distribution of the six elements in different parts of a few species of plants.

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MATERIALS AND METHODS

An area in central Pennsylvania, which falls within the region of the podzols and the gray-brown podzolic soils, was investigated. Soils within the area show very close relationship with the rock formations. The soils developed from noncalcareous shales or sandstones are strongly acid, whereas those derived from limestones are less acid, and in certain eroded spots may be alkaline. The acid soils include gray-brown podzolic, peat, and undeveloped acid soils. The calcium-saturated soils consist of neutral limestone and calcareous alluvial soils in the limestone region. Because acid soils are dominant in the area, the trees, shrubs, herbaceous plants, and ferns are mostly of the calcifugous type. Only very few calcicolous plants have been found, and these are on limestone outcrops or on the narrow stream bank where calcareous alluvial soils occur.

Plants of 31 species, including ferns, clubmosses, and flowering plants on natural soils, together with corn and alfalfa plants in cultivated fields, were used for the studies. The plants under investigation include the following three groups (55, 56):

I. Calcifugous Plants

1. Running clubmoss (*Lycopodium clavatum*)
2. Running-pine (*Lycopodium flabelliforme*)
3. Round-branch groundpine (*Lycopodium obscurum*)
4. Hay-scented fern (*Dennstaedtia punctilobula*)
5. Interrupted fern (*Osmunda claytoniana*)
6. Spotted Pipsissewa (*Chimaphila maculata*)
7. Trailing arbutus (*Epigaea repens*)
8. Huckleberry (*Gaylussacia baccata*)
9. True wintergreen (*Gaultheria procumbens*)
10. Mountain laurel (*Kalmia latifolia*)
11. Great laurel (*Rhododendron maximum*)
12. Sweet blueberry (*Vaccinium pennsylvanicum*)
13. Lowbush blueberry (*Vaccinium vacillans*)
14. Sweet fern (*Myrica asplenifolia*)

II. Calcicolous Plants

15. Bulblet fern (*Cystopteris bulbifera*)
16. Hairy cliff brake (*Pellaea atropurpurea*)
17. Common milkweed (*Asclepias syriaca*)
18. Teasel (*Dipsacus sylvestris*)
19. Alfalfa (*Medicago sativa*)
20. Peppermint (*Mentha piperita*)
21. Spearmint (*Mentha spicata*)

III. Plants Indifferent to Soil pH, and Unclassified Plants

22. Marginal woodfern (*Dryopteris marginalis*)
23. Elderberry (*Sambucus canadensis*)
24. Corn (*Zea mays*)
25. Christmas fern (*Polystichum acrostichoides*)
26. Yarrow (*Achillea millefolium*)
27. Joe-Pye weed (*Eupatorium maculatum*)
28. Boneset (*Eupatorium perforliatum*)
29. Joe-Pye (*Eupatorium fistulosum*)
30. Columbine (*Aquilegia canadensis*)
31. Southern beechfern (*Phegopteris hexagonoptera*)

The plants were collected during the middle of July 1948. The plant samples were dried for about 48 hours at a temperature of 60 to 70°C. in a large oven and then ground. Each sample was ashed in a Pyrex beaker at approximately 550°C. overnight. A small amount of carbon usually present after ashing was destroyed by perchloric acid and nitric acid digestion. The calcium and potassium were determined by use of a flame photometer (53). Aluminum, iron, manganese, and phosphorus were determined colorimetrically by means of the Coleman spectrophotometer. Aluminum was determined by the aluminon method (44, 60) slightly modified by the senior author. Iron was determined by the *o*-phenanthroline method described by Saywell and Cunningham (48). Manganese was determined by the simlpified periodate method (57). Phosphorus was determined by an adaptation of the method of Fiske and Subbarow (14).

All the soil samples collected in this work were taken near the roots of the plants examined. To help in evaluation of sites, easily extractable aluminum, iron, manganese, phosphorus, calcium, and potassium, replaceable hydrogen, and pH of the soils were determined (44) Only the pH values of the soils are reported in this paper.

RESULTS AND DISCUSSION

Chemical characteristics of calcifugous and calcicolous plants

Analyses of the calcifugous and calcicolous plants are shown in tables 1 and 2.

Aluminum content. Though most calcifuges do not contain unusual amounts of aluminum, the percentage of this element in one genus studied, namely, *Lycopodium*, is significantly high. The Al content of plants of this genus varies from 0.079 to 0.793 per cent on the dry basis, or from 2.43 to 15.75 per cent on the ash basis. These findings are in agreement with those of Hutchinson and Wollack (27), who referred to these plants as "biological accumulators of aluminum." Without consideration of the plants collected in site 2, in which contamination from dust was possible, the aluminum content of the remaining calcifuges is not found to be exceptional, namely, from 0.013 to 0.047 per cent. Among the calcicoles, the aluminum content does not differ markedly from that of the calcifuges other than *Lycopodium*, namely, from 0.013 to 0.034 per cent.

Iron content. Most calcifuges, with the exception of a few specimens in which contamination from dust is suspected, do not have an unusually high iron con-

TABLE 1

Al, Fe, Mn, P, Ca, and K content of calcifugous plants

Dry-weight basis

PLANT	SITE NO.*	SOIL pH	PLANT PART ANALYZED	CRUDE ASH	Al	Fe	Mn	P	Ca	K
				%	%	%	%	%	%	%
1. Running clubmoss	4	4.1	Whole	4.25	0.263	0.028	0.032	0.14	0.12	1.20
	10	3.3	Whole	3.25	0.079	0.017	0.037	0.11	0.10	1.03
2. Running-pine	13	3.8	Whole	5.02	0.793	0.015	0.010	0.12	0.07	1.20
	11	3.5	Whole	4.79	0.761	0.011	0.023	0.14	0.05	1.15
3. Round-branch ground-pine	14	3.9	Whole	3.07	0.329	0.024	0.012	0.13	0.12	0.84
	10	3.3	Whole	3.34	0.169	0.017	0.016	0.09	0.10	0.59
	12	4.0	Whole	3.20	0.371	0.011	0.019	0.15	0.08	0.86
4. Hay-scented fern	15	4.2	Pinnae	9.00	0.047	0.033	0.052	0.18	0.49	2.50
			St. & Rt.†	5.01	0.026	0.012	0.017	0.16	0.18	1.68
	14	4.8	Pinnae	9.78	0.040	0.045	0.052	0.25	0.36	2.91
	11	3.4	Pinnae	9.53	0.028	0.017	0.296	0.19	0.50	3.31
			St. & Rt.†	5.00	0.005	0.003	0.095	0.12	0.13	1.96
5. Interrupted fern	16	5.3	Pinnae	8.90	0.034	0.010	0.117	0.44	0.69	2.59
6. Spotted Pipsissewa	9	4.5	Leaves	5.49	0.024	0.009	0.022	0.19	1.05	0.97
			Stems	7.01	0.017	0.010	0.183	0.14	1.35	1.18
			Roots	5.02	0.017	0.005	0.056	0.15	0.72	1.30
7. Training arbutus	13	3.9	Leaves	3.38	0.014	0.009	0.182	0.10	0.77	0.65
8. Huckleberry	3	3.6	Leaves	3.97	0.018	0.011	0.037	0.08	0.87	0.72
	8	3.4	Leaves	4.51	0.029	0.019	0.058	0.11	0.73	0.74
9. True wintergreen	9	4.5	Leaves	4.34	0.020	0.011	0.033	0.13	0.72	0.86
			Stems–roots	2.11	0.013	0.006	0.055	0.11	0.44	0.32
	12	3.9	Leaves	4.59	0.021	0.007	0.104	0.13	0.85	0.80
			Stems–roots	2.58	0.013	0.004	0.085	0.11	0.44	0.49
10. Mountain laurel	3	3.6	Leaves	3.68	0.009	0.006	0.041	0.10	0.74	0.67
	8	3.4	Leaves	4.47	0.014	0.009	0.096	0.11	0.90	0.66
11. Great laurel	17	4.2	Leaves	4.45	0.019	0.015	0.123	0.09	1.09	0.39
	18	3.9	Leaves	4.92	0.016	0.012	0.082	0.07	1.07	0.65
12. Sweet blueberry	2‡	4.3	Leaves	3.36	0.081	0.053	0.307	0.11	0.56	0.24
	19	3.9	Leaves	3.88	0.020	0.010	0.314	0.09	0.78	0.45
	20	4.2	Leaves	3.48	0.023	0.010	0.436	0.10	0.57	0.34
			Stems	1.75	0.015	0.009	0.227	0.08	0.33	0.18
			Roots	1.41	0.022	0.013	0.135	0.11	0.24	0.16
13. Lowbush blueberry	2‡	4.4	Leaves	3.32	0.039	0.030	0.099	0.09	0.67	0.36
	3	3.6	Leaves	4.17	0.021	0.004	0.059	0.10	0.96	0.48
	9	4.6	Leaves	4.40	0.036	0.016	0.138	0.09	0.75	0.66
			Stems	2.52	0.013	0.006	0.148	0.07	0.64	0.21
			Roots	1.21	0.015	0.008	0.121	0.14	0.15	0.17

TABLE 1—*Concluded*

PLANT	SITE NO.*	SOIL pH	PLANT PART ANALYZED	CRUDE ASH	Al	Fe	Mn	P	Ca	K
				%	%	%	%	%	%	%
14. Sweet fern	2‡	4.5	Leaves	3.70	0.108	0.392	0.045	0.12	0.44	0.64
	21	4.3	Leaves	2.86	0.020	0.023	0.023	0.09	0.50	0.76
	20	4.5	Leaves	3.51	0.025	0.021	0.176	0.10	0.48	0.52
			Stems	1.98	0.009	0.006	0.092	0.03	0.49	0.15
			Roots	2.34	0.020	0.005	0.135	0.06	0.54	0.21

* Sites 3, 4, 8, 9, 11, 12, 13, 17, 18, 19, 20, and 21 are gray-brown podzolic soils derived from acid sandstones; sites 2, 14, 15, and 16, acid roadside-soils; site 10 is an acid peat soil.

† Stipes and rootstocks.

‡ Plants possibly contaminated with dust.

TABLE 2

Al, Fe, Mn, P, Ca, and K content of calcicolous plants

Dry-weight basis

PLANT	SITE NO*	SOIL pH	PLANT PART ANALYZED	CRUDE ASH	Al	Fe	Mn	P	Ca	K
				%	%	%	%	%	%	%
15. Bulblet fern	6	7.9	Pinnae	12.20	0.034	0.037	0.004	0.18	1.86	1.73
16. Hairy cliff brake	22	7.9	Pinnae	6.65	0.022	0.021	0.002	0.14	0.59	1.66
17. Common milkweed	7	7.8	Leaves	13.95	0.021	0.017	0.006	0.42	2.27	2.93
18. Teasel	1	8.0	Leaves	12.12	0.014	0.019	0.005	0.54	2.09	2.74
	23	7.0	Leaves	9.99	0.014	0.014	0.006	0.44	1.82	1.98
	24	6.9	Leaves	12.39	0.019	0.013	0.009	0.35	1.97	3.16
	24	6.7	Leaves	13.30	0.019	0.015	0.005	0.47	2.13	3.08
19. Alfalfa	25	5.9	Leaves	9.19	0.013	0.015	0.005	0.27	1.80	1.61
20. Peppermint	7	7.8	Leaves	12.52	0.021	0.025	0.006	0.47	1.98	2.86
21. Spearmint	26	6.2	Leaves	10.84	0.029	0.026	0.007	0.46	1.78	2.63
	7	8.0	Leaves	12.15	0.022	0.019	0.006	0.52	1.57	3.26

* Sites 1 and 7 are calcareous alluvial soils; sites 6, 23, and 24, limestone soils; site 25, is a field soil; site 26, a roadside-soil with limestone chips.

tent as compared with calcicoles. Several species, such as sweet fern, sweet blueberry, and lowbush blueberry on site 2, are found to contain abnormally large amounts of iron as compared with the same plants growing on equally acid soils in other sites. Since site 2 is a roadside soil near an iron-ore area, these high-iron results are likely due to contamination with dust which was either absorbed or merely adhered to the leaves. Except for these possible cases of contamination, the iron contents of the calcifuges, ranging from 0.009 to 0.045 per cent, do not differ significantly from those of the calcicoles, which range from 0.013 to 0.037 per cent.

Manganese content. Obviously, the manganese content of most calcifugous plants, except for the aluminum-accumulators, is consistently high ranging from 0.033 to 0.436 per cent. It is noteworthy that one manganese-accumulator has been discovered: it is sweet blueberry which contains 0.307 to 0.436 per cent of Mn in the leaves on the dry basis, or 8.09 to 12.51 per cent on the ash basis. On the other hand, the percentage of manganese is significantly low in all calcicoles, ranging from 0.002 to 0.009 per cent.

Phosphorus content. With the exception of interrupted fern, the percentage of phosphorus of most calcifuges is comparatively low, varying from 0.07 to 0.19 per cent. Conversely, a majority of calcioles, except for hairy cliff brake, contain rather large amounts of phosphorus, ranging from 0.18 to 0.54 per cent.

Calcium content. In general, the calcicoles have a higher percentage of calcium than do the calcifuges, but the latter are not necessarily very low in calcium. With the exception of hairy cliff brake, the calcicoles studied contain about 1.57 to 2.27 per cent of Ca, whereas the calcifuges, except for the aluminum-accumulators, which have an extremely low content of calcium, contain about 0.48 to 1.08 per cent. It may be that in the physiology of the aluminum-accumulators the absorption of calcium is depressed by the high intake of aluminum.

Potassium content. There is no striking difference existing between the calcifuges and calcicoles with respect to their potassium content. The calcifuges studied range between 0.24 and 3.31 per cent of K, whereas the calcicoles studied range from 1.61 to 3.26 per cent of K. The potassium content of calcicoles in general is uniformly higher, however, than that of calcifuges. These findings do not support the views of certain investigators (1,47), who maintain that plants would have difficulty in obtaining potassium from calcareous soils.

Ash content. The percentage of crude ash, in general, is significantly higher in calcicoles than in calcifuges, the former ranging from 6.65 to 13.95 per cent and the latter from 3.07 to 9.78 per cent.

On the basis of the aforementioned chemical characteristics of the plants examined, it appears that it is not difficult for the calcifuges to obtain calcium from strongly acid soils, or for calcicoles to take potassium from calcium-saturated soils. Furthermore, no differences of any significance have been found to exist between the calcifuges and calcicoles in their intake of iron. A tentative suggestion as to why different plants have different pH preferences is made as follows:

Certain aluminum-accumulating calcifuges such as *Lycopodium* may have heavy requirements for aluminum. Hence, the distribution of those calcifuges is likely to be associated with the aluminum supply of the acid soils, in which this element is highly available (11, 37).

Possibly, most calcifuges require or at least tolerate larger amounts of manganese than do the calcicoles. The distribution of such calcifuges, confined to acid soils, may be related to the manganese supply that is always available in such soils (13, 20). On the other hand, the reason why the calcicoles cannot thrive on strongly acid soils may well be that the relatively high soluble manganese may be toxic to these plants.

The phosphorus content of plants is probably associated with the development of the phosphate-buffer system. Phosphates have low buffer capacity in the acid range pH 3.5 to 5.5, and a high capacity in the circum-neutral range, pH 6.0 to 7.5 (51). This may constitute a fundamental difference between calcicoles and calcifuges—the former can survive in circum-neutral soils, whereas the latter cannot. The low phosphate-buffer capacity in calcifuges makes them unable to tolerate neutral soil conditions (51).

Chemical composition of plants in relation to soil pH

The chemical composition of plants indifferent to soil pH and of unclassified plants is presented in table 3.

Aluminum. Even though the so-called aluminum-accumulators have been found on acid soils, but not on neutral or alkaline soils, little correlation has been found to exist between the aluminum content of plants and the soil pH, so far as the same species growing on different soils is concerned. These findings are in harmony with those of Fried and Peech (16), Hoffer and Trost (24), and Shear (49), who found no consistent correlation existing between the liming of the soil and the aluminum intake by plants. In a number of plants, however, the aluminum content is closely associated with the supply of aluminum in the soil. This correlation is clearly shown in running clubmoss and round-branch groundpine (table 1), which contain much larger amounts of aluminum when growing on the gray-brown podzolic soil than on the peat soil. The peat soil is considered to have a poor supply of aluminum (37), and actually contains a very small amount of easily extractable aluminum according to a soil analysis, not presented here.

Iron. It is generally considered that an increased pH of the soil decreases the solubility of the iron in the soil to the point of deficiency (54). This assumption is based largely on the results of solution culture experiments, and the application of the results to soil conditions is by inference and without direct experimental support (58).

According to tables 1, 2, and 3, there apparently is no certainty that the low pH of the soil increases the availability of iron to the plant. Among the calcifuges and calcicoles there is no apparent relationship between intake of iron and soil pH. The indifferent plants, with the exception of the possible cases of contamination, have a higher intake of iron when growing on less acid or neutral soil than on the more acid soil. These findings support those of numerous investigators (4, 6, 24, 25) who found that the iron content of various plants was increased by liming the soil. The observation can be explained by the fact that ferrous iron is soluble under more alkaline conditions than is ferric iron (30).

The availability of iron to plants is a complex problem. The solubility of iron in soil may be influenced not only by the pH, but also by the intensity of the oxidation-reduction system (58), or the presence of organic matter or other reducing material (30), the amount of potentially available iron such as free iron oxide (42), and the amount of available manganese (30). Different combinations of these factors would afford an explanation of why no consistent relation has been found between the soil pH and the iron intake by plants.

Manganese. Obviously, the manganese content of plants is rather definitely correlated with soil pH. The plants of the three groups show the same general trend, namely, the percentage of manganese in plants increases as the soil pH decreases. Among the indifferent plants, the amount of manganese is about three to ten times as great on the strongly acid soil as on less acid or neutral soil. In this connection, the chlorosis and stunted growth of corn plants grown on the strongly acid soil of the central row of Jordan plot 32 (site 32) have been found to be associated with an excessive absorption of manganese but not of aluminum or iron. The amount of manganese in corn plants grown on that soil

TABLE 3

Al, Fe, Mn, P, Ca, and K content of plants indifferent to soil pH and unclassified plants
Dry-weight basis

PLANT	SITE NO.*	SOIL pH	PLANT PART ANALYZED	CRUDE ASH	Al	Fe	Mn	P	Ca	K
				%	%	%	%	%	%	%
22. Marginal woodfern	27	4.9	Pinnae	7.39	0.022	0.009	0.037	0.31	0.77	2.04
	28	6.3	Pinnae	7.34	0.023	0.022	0.004	0.23	0.87	1.97
23. Elderberry	29†	4.0	Leaves	8.59	0.055	0.076	0.038	0.11	1.59	1.23
	30	5.5	Leaves	9.31	0.018	0.013	0.013	0.33	1.43	2.20
	31	6.3	Leaves	10.03	0.039	0.029	0.016	0.34	1.62	1.88
24. Corn	32	3.7	Leaves	6.17	0.028	0.023	0.119	0.23	0.50	1.79
	33	5.0	Leaves	8.98	0.021	0.016	0.013	0.22	0.71	2.64
	34	8.1	Leaves	6.09	0.026	0.024	0.012	0.27	1.05	0.47
25. Christmas fern	4	4.1	Pinnae	8.26	0.024	0.008	0.038	0.28	0.48	2.44
	35	6.7	Pinnae	7.62	0.019	0.016	0.004	0.30	0.67	2.18
	35	6.8	Pinnae	7.62	0.032	0.014	0.003	0.21	0.67	2.26
26. Yarrow	2†	4.4	Leaves	12.15	0.051	0.099	0.016	0.29	1.06	2.88
	37	5.5	Leaves	12.91	0.022	0.022	0.006	0.19	1.27	2.22
	36	7.4	Leaves	13.81	0.024	0.019	0.006	0.34	1.22	4.07
27. Joe-Pye weed	7	7.8	Leaves	13.95	0.027	0.021	0.004	0.35	2.30	2.00
28. Boneset	5†	5.7	Leaves	14.46	0.130	0.099	0.049	0.23	1.50	2.34
29. Joe-Pye	5	5.7	Leaves	13.41	0.036	0.032	0.026	0.24	1.84	2.27
30. Columbine	6	7.9	Leaves	11.66	0.011	0.009	0.004	0.19	2.18	2.37
31. Southern beechfern	16	5.4	Pinnae	11.72	0.023	0.017	0.010	0.28	0.98	2.59

* Sites 4 and 27 are gray-brown podzolic soils derived from sandstones; sites 2, 5, 29, 30, and 31, acid roadside-soils; sites 6, 28, and 35, limestone soils; site 32, central row of Jordan plot 32, Pennsylvania State College; site 33, edge of Jordan plot 32; site 34, Jordan plot 23.

† Plants possibly contaminated with dust.

is nearly ten times as great as that of plants grown on the moderately acid soil near the edge of the plot (site 33) and on the alkaline soil of plot 23 (site 34). These findings are in harmony with the observations of many investigators (7, 9, 10, 16, 17, 20, 23, 29, 36, 38, 40, 49) who have reported a decrease of manganese in plants grown on calcareous or limed soil as compared to those grown on acid soil.

Several investigators have explained why the availability of manganese is fairly high in acid soil conditions. Leeper (34) suggested three basic forms of manganese existing in the soil from the standpoint of availability to the plant; namely, manganous, colloidal hydrated, and inert manganic Mn. All forms are in dynamic equilibrium. This equilibrium tends toward formation of the manganous form under acid soil condition, whereas, under alkaline condition it favors oxidation to the manganic form (17). This suggestion is based on the fact that auto-oxidation of manganous hydroxide takes place in a basic medium (41). Furthermore, Gerretsen (18) asserted that the precipitation of insoluble manganese dioxide in soil is caused by specific microorganisms which prefer the pH limits of 6.5 to 7.8. In addition, Leeper (34) has said that, under aerated conditions, the manganous Mn is almost all removed from neutral or alkaline soils, since bacterial oxidation is rapid, and reduction by organic matter is very low. On the other hand, this bivalent form of Mn is favored in strongly acid soils, as bacterial oxidation is very slow or absent, whereas organic matter can reduce the higher oxides.

Phosphorus. The results, in general, show a fairly significant correlation between the phosphorus content of plants of all three groups and the pH of the soil. In most instances, percentage of phosphorus in plants growing on soil with a high pH is greater than that in plants on soil with a low pH. These findings agree with the observations of numerous workers (9, 11, 12, 15, 22, 52, 59) that plants grown on limed soil obtain more phosphorus than those on unlimed soil.

Calcium. The calcifuges show no general relationship between calcium intake and soil pH. Among the indifferent plants, however, there is a close relation between calcium content and soil pH. That the influence of the soil pH on the calcium content of calcifuges and calcicoles is highly variable agrees with the observations of Bryan (8) and of Smith and Hester (52). On the contrary, the results showing that the indifferent plants have greater amounts of calcium on neutral or nearly neutral soil than on more acid soil support the findings of many investigators (5, 6, 9, 16, 19, 35, 40, 45, 50). These controversial results reveal that plant species differ in their relationship between intake of calcium and soil pH.

Potassium. The influence of soil pH on the absorption of potassium by plants is a highly controversial subject, as reviewed by Peech and Bradfield (43). As a whole, in this investigation no definite relationship has been found to exist between soil pH and potassium intake. The inconsistent results can be explained by the fact that the ability of a plant to obtain potassium from the soil is influenced not only by soil pH but by the amounts and forms of potassium in the soil, the concentration of other ions present, and the plant species studied (46).

Selective absorption of different elements by plants growing in close proximity

In the present investigation no attempt was made to compare the selective absorption of plants of all 31 species, the object being simply to determine characteristic differences in absorption of different elements of some species which grew side by side on the same natural soil. This investigation was confined to the plants found in sites 1 to 12. In a comparison of the ability of different plants to obtain the six elements from the same natural soil, the following facts are revealed:

On the calcareous alluvial soils of sites 1 and 7 the selective action of the two calcicoles, teasel (plant 18) and peppermint (plant 20), seems not markedly different. They both absorbed comparatively high amounts of phosphorus, calcium, and potassium, but a rather small quantity of manganese. Likewise, there is little difference in the intake of aluminum and iron between the two plants.

Growing on the strongly acid soil of site 2, the three calcifuges sweet blueberry, lowbush blueberry, and sweet fern apparently absorbed much greater amounts of manganese than did the indifferent plant, yarrow: sweet blueberry (plant 12) obtained about twenty times as much; lowbush blueberry (plant 13), six times as much; and sweet fern (plant 14), three times as much. On the other hand, yarrow (plant 26) obtained two to three times as much phosphorus, about twice as much calcium, and four to twelve times as much potassium as did the three calcifuges on the same site.

Among the three calcifuges that grew on the very strongly acid soil in site 3, huckleberry (plant 8) and lowbush blueberry (plant 13) absorbed about twice as much aluminum as did mountain laurel (plant 10), whereas huckleberry took up about twice as much iron as did the other two species. Slight differences in selective absorption of manganese, calcium, and potassium, and almost no difference in absorption of phosphorus occurred among the three species.

On the strongly acid soil in site 4 the calcifuge running clubmoss (plant 1) obtained about eleven times as much aluminum and almost four times as much iron, but only half as much phosphorus and potassium, and fourth as much calcium as did Christmas fern (plant 25) which is an indifferent species. The intake of manganese by these two plants on this strongly acid soil is similar.

The results show that on the acid roadside soil of site 5, boneset (plant 28) absorbed about three and a half times as much aluminum, three times as much iron, and twice as much manganese as did Joe-Pye weed (plant 29). The absorption capacity for phosphorus, calcium, and potassium of the two species seems rather uniform.

In site 6, the two species growing on the calcareous lime-stone soil behaved similarly toward manganese. Nevertheless, bulblet fern (plant 15) had about three times as much aluminum, four times as much iron, and a slightly greater amount of calcium and potassium than did columbine (plant 30). The three species Joe-Pye weed (plant 27), peppermint (plant 20), and common milkweed (plant 17), which grew on the calcareous alluvial soil of site 7, behaved some what similarly toward the absorption of the six elements, although they differed more or less toward that of calcium and potassium.

On the strongly acid soil of site 8, huckleberry (plant 8) obtained about twice as much aluminum and iron as did mountain laurel (plant 10), whereas the latter species absorbed twice as much manganese as the former. The behavior of these two calcifuges toward the absorption of phosphorus, calcium, and potassium was rather uniform.

On the strongly acid soil of site 9 there was obviously a significant difference in the absorption capacity for manganese among the three calcifuges. Lowbush blueberry (plant 13) accumulated about four to six times as much manganese, respectively, as did true wintergreen (plant 9) and spotted Pipsissewa (plant 6). No significant differences in absorption capacity for the remaining elements have been found among the three species.

In site 10, the two species of *Lycopodium* maintained fairly high ability to absorb aluminum even though growing on aluminum-deficient acid peat soil. It is again shown that the absorption power of round-branch groundpine (plant 3) for aluminum was about two and one-half times as great as that of running clubmoss (plant 1), although both plants grew on exactly the same peat soil. The latter species, however, obtained twice as much manganese and potassium as the former. No distinct differences have been found existing between the two species concerning the absorption for iron, phosphorus, and calcium.

It is remarkable that on the strongly acid soil of site 11 the two calcifuges behaved entirely differently toward the absorption for manganese, aluminum, calcium, and potassium. Running-pine (plant 2) took up about twenty-five times as much aluminum as did hay-scented fern (plant 4), whereas the latter obtained twelve times as much manganese, ten times as much calcium, and three times as much potassium as did the former. There was no significant difference in the absorption of iron and phosphorus between the two species.

In site 12, it is also shown that the two calcifuges maintained a different ability to absorb aluminum, manganese, and calcium. Round-branch groundpine (plant 3) absorbed eighteen times as much aluminum as did true wintergreen (plant 9), whereas the latter had five times as much manganese, and ten times as much calcium as the former. No distinct differences are seen between the two species in absorption of iron, phosphorus, and potassium.

The data obtained in the present investigation are too incomplete to give a comprehensive picture of the selective absorption of plants examined or to show the correlation of the selective absorption of the calcifuges and of the calcicoles. A few observations can, however, be made. It is apparent that plants of different species varied greatly in their ability to absorb different elements when growing on the same natural soil. In the cases examined, it is evident that the calcifuges had a greater ability to absorb either aluminum or manganese than did the indifferent plants. Among the calcifuges, the *Lycopodium* species maintained a high absorption capacity for aluminum but a low capacity for manganese and calcium in comparison with other calcifuges. Likewise, this ability varied with the species. On the other hand, the remarkably high absorption of manganese by blueberries seems rather evident.

The two indifferent plants yarrow and Christmas fern took up greater amounts of phosphorus, calcium, and potassium than did the calcifuges that grew in close proximity. The absorption capacity of the calcicoles toward the six elements examined seems rather uniform. They had a generally similar tendency to absorb rather high quantities of phosphorus, calcium, and potassium, but small amounts of manganese.

This preliminary investigation clearly shows that, in addition to soil conditions, the species or heredity of the plant is an important factor affecting the mineral composition of the plant.

Distribution of Al, Fe, Mn, P, Ca, and K in different parts of certain plants

The distribution of aluminum, iron, manganese, phosphorus, calcium, and potassium in different parts of the following six calcifuges was examined:

Plant No.	*Common name*	*Site No.*
4	Hay-scented fern	11, 15
6	Spotted Pipsissewa	9
9	True wintergreen	9, 12
12	Sweet blueberry	20
13	Lowbush blueberry	9
14	Sweet fern	20

The analyses of these plants are given in table 1.

Aluminum. The data presented show that hay-scented fern contained more aluminum in the pinnae than in the stipes and rootstocks and that, likewise, the remaining five species accumulated more aluminum per unit dry weight in leaves than in roots and stems. These findings do not support the conclusion of Hutchinson (26, 28) that accumulation of aluminum in a number of acid-loving plants such as *Vaccinium*, *Gaultheria*, *Myrica*, and *Rhododendron* occurs in the roots but not necessarily in the aerial parts.

Iron. With the exception of sweet blueberry, which accumulated more iron in roots than in leaves and stems, the species showed a proportionately greater amount of iron in the dry leaves than in roots and stems.

Manganese. In spotted Pipsissewa, true wintergreen, and lowbush blueberry, much more manganese was accumulated in stems than in roots and leaves, whereas sweet blueberry and sweet fern contained more manganese in the leaves than in stems and roots; likewise, hay-scented fern contained more manganese in pinnae than in stipes and rootstocks. These findings confirm those of Kelley (31) that the distribution of manganese in the different parts of plants varies in different species. He found manganese to be present in greater abundance in stems of guava and peanut plants, but not in other plants.

Phosphorus. In the two species of blueberries, more phosphorus was accumulated in roots than in leaves and stems, whereas sweet fern appeared to accumulate more phosphorus in leaves than in other parts of the plant. Spotted Pipsissewa, true wintergreen, and hay-scented fern had a rather uniform distribution of phosphorus throughout the plant body.

Calcium. More calcium was found to be accumulated in leaves than in stems and roots of true wintergreen, sweet blueberry, and lowbush blueberry. Likewise, hay-scented fern accumulated more calcium in pinnae than in stipes and rootstocks. On the other hand, spotted Pipsissewa contained more calcium in stems than in leaves and roots. The distribution of calcium in sweet fern seems rather uniform, however, although slightly greater amounts appeared in roots.

Potassium. With the exception of spotted Pipsissewa, these species accumulated much more potassium in aerial parts than in roots.

From the investigation it is clearly seen that different parts of the plant contained varying amounts of the same elements, and that the distribution of certain elements in the plant body varied with the species.

SUMMARY

To ascertain why plants of certain species thrive on soils of certain pH ranges, 31 species of native and cultivated plants, including calcifugous, calcecolous, and indifferent species were studied. In July mature representative leaves were taken from each species studied. The leaf tissue was dried, pulverized, ashed, and analyzed for total aluminum, iron, manganese, phosphorus, calcium, and potassium. Soil samples, taken from around the roots of each plant were analyzed for replaceable calcium, magnesium, potassium, manganese, aluminum, and iron. The pH and easily extractable phosphorus was also determined.

The aluminum content of most calcifugous plants was not notably different from that of calcicolus plants with the exception of the *Lycopodium* species (club mosses). The latter were exceptionally high in aluminum. This finding is in agreement with the observations of Hutchinson and Wollack (27) who referred to *Lycopodium* species as "biological accumulators of aluminum." With the exception of the "accumulators," the aluminum content of calcifuges ranged from 0.013 to 0.047 per cent and that of the calcicoles ranged from 0.013 to 0.037 per cent.

Manganese, on the other hand, proved to be definitely related to soil pH and plant type. It was low in the calcicoles and high in the calcifugous plants. The amounts in the tissues were related to the amounts easily extractable from soils. Calcicoles contain 0.002 to 0.009 per cent, whereas calcifuges contain 0.003 to 0.436 per cent of Mn. The blueberry is notable for its high content of manganese.

There is no evidence that iron is more abundant in calcifugous plants than in calcicoles.

Although the calcicolous were found to have slightly higher calcium contents than the calcifugous plants, nevertheless, the latter cannot be considered to be low in this element. The calcicoles contained 1.56 to 2.27 per cent calcium, and the calcifuges 0.48 to 1.08 per cent.

Potassium is somewhat higher in calcicolous plants, but the difference is small. The calcicoles ranged from 1.61 to 3.20 per cent K, and the calcifuges from 0.24 to 3.31 per cent. Lime-loving plants appeared to have no difficulty in obtaining sufficient potassium from calcium-saturated soils.

Calcifugous plants were generally low in phosphorus, and calcicolous plants high in this element. The former contained 0.07 to 0.19 per cent, and the latter

0.18 to 0.54 per cent phosphorus. Very acid soils seldom contain more than a trace of easily extractable phosphorus.

Corn from three sites in close proximity having pH values of 3.7, 5.0, and 8.1 was found to differ very little in aluminum or iron content but to differ markedly in manganese, from 0.119 to 0.013 to 0.012 respectively for the three sites. The corn growing on the site with pH 3.7 was chlorotic and stunted; it never reached more than 12 inches in height.

Evidence is presented showing that different plants growing in close proximity differ considerably in the relative uptake of the different elements.

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A HAMMER-DRIVEN SOIL-CORE SAMPLER

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Three types of soil-core samplers are in general use. In each, a cutting head is turned, hammer-driven, or pushed to cut a sample from the soil into a cylindrical container with a minimum of disturbance to soil structure. Baver (1, pp. 174–175) pointed out that not only the method of sampling but the core size is important in obtaining undisturbed cores and recommended a diameter no smaller than 3 inches. The present writers have been unable to find or develop a technique that will take cores smaller than about 3 inches in diameter without serious compression or disturbance in heavy, compact, or plastic soils. Also, because of soil variation, more small than large cores are necessary to characterize porosity differences due to soil treatment. Ward (6) found 600-cc. cores somewhat superior to 60-cc. cores in soil porosity studies. As doubling both diameter and height of the sample taken will increase the volume eight times, a relatively small increase in dimensions may greatly increase the effectiveness of a core sampler.

The machine of Kelley, Hardman, and Jennings (2) and the tool designed by Lutz (3) have been tested in an effort to find a suitable core-sampling technique for small plots.

Although the former seemed well suited to taking deep samples, it proved disappointing in the shallow sampling of small plots. It could not be moved into plots over plants such as cotton or corn without damage and, though much faster and superior to the pit method of monolith sampling, this machine is too slow and cumbersome for routine shallow sampling.

The tool of Lutz has seemed satisfactory in loose friable soils, but could not be forced into hard, dry, or sticky compact soil without compressing or fracturing the core. This was more noticeable with the model using the sleeve and removable cutting head than with the one using the can with its rim acting as cutting edge. The latter has a sharper bevel and hence offers less resistance to penetration. It is unlikely that a cutting edge can be made which will not, to some noticeable degree, compress the wall of a sample core. As the core diameter is decreased, a size will be reached where this compression will seriously disturb the whole sample. Instead of the core being cut free so as to slide into the cylinder, it will act as a plug to the opening and the soil will be compressed downward and outward below the cutting edge.

The can model sampler of Lutz has some highly desirable features. Should the cutting edge of the can be crumpled on a stone, the sampler may be unharmed. It is a simple matter to replace the inexpensive damaged can with another. This sampler is a compact, one-piece unit that is easily carried and

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[1] Auburn, Alabama.

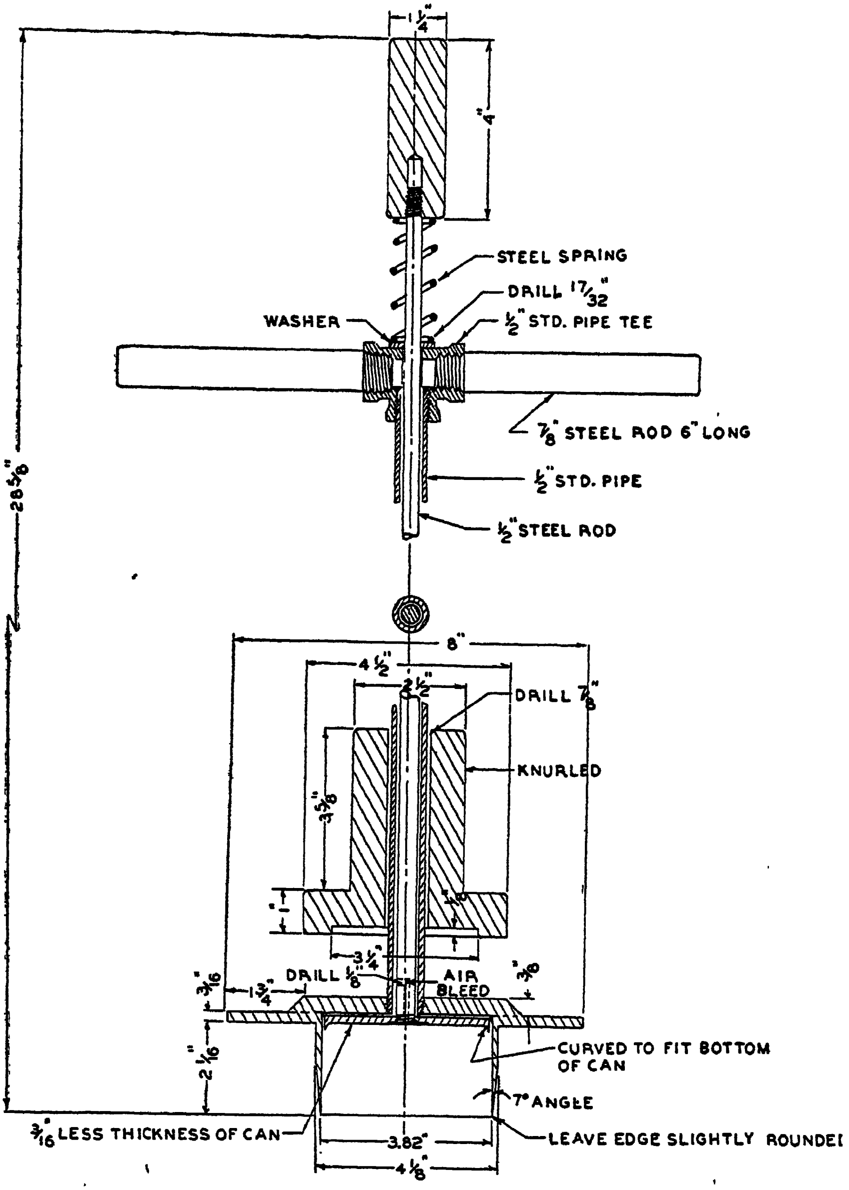

FIG. 1. SLIDING HAMMER SOIL-CORE SAMPLER IN DETAIL

convenient to use. These features were combined with the sliding-hammer principle used by Veihmeyer (5) and Uhland[2] in developing the sliding-hammer modified Lutz sampler now used for soil porosity and compaction studies by the writers.

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[2] Uhland, R. E. Procedure for taking core samples with core sampler. Report to Soil Conservation Service, U. S. Dept. Agr., October 2, 1947. (Mimeographed.)

DESCRIPTION OF SLIDING-HAMMER SAMPLER

The new sampler is little more than an enlarged-can-model Lutz sampler with the addition of a sliding hammer to drive the cutting edge of the sample can into a compact soil (figs. 1 and 2). The containers used are about 3$\frac{3}{4}$ inches in diameter and 2$\frac{9}{16}$ inches high (volume of 470 cc.)[3] In the can bottom a $\frac{1}{8}$ inch hole is drilled, which together with relief channels and a hole in the plunger of the sampler, allows the air to escape readily as the can is being driven into the soil. The hole in the can also allows the operator to see whether the can is filled. The plunger is shaped to fit the bottom of the can to prevent buckling of the can when it is driven into compact or hard, dry soil. In operation, a can is inverted and slipped into the cup of the sampler and the lid removed. The soil surface at the sample depth desired is cut level with a sharp spade or trowel. The sampler is held upright with the cutting edge resting on the soil surface, and the hammer is raised to the top of the slide bar and allowed to drop freely to drive the sampler downward into the soil. The sharp edge of the can and the beveled edge of the cup compress the soil outward as it is cut away from the relatively undisturbed sample. A sufficient number of blows are given to drive the shoulder flush with the soil surface. Since this shoulder is even with the inside bottom of the inverted sample can, the can should be just filled with undisturbed soil. The shoulder rim is made wide to minimize compression if the last blow tends to drive the can below full depth. If the soil is moist and relatively loose, the sampler may be pushed into the soil. The sampler is next removed from the sample-filled can by pressing downward on the plunger handle with one hand while pulling up on the hammer slide bar with the other. Frequently a little soil between the beveled edge of the cup and the can will cause binding. A gentle upward tap with the sliding hammer on the slide bar cap, while firm pressure is maintained on the plunger, will release the sampler. After the sampler is removed, the can with the sample is spaded from the soil and the

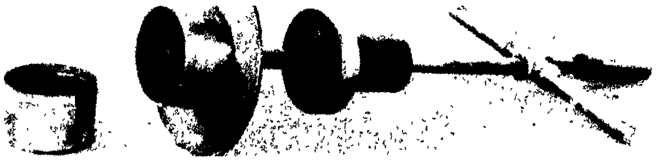

FIG. 2. SLIDING HAMMER SOIL-CORE SAMPLER WITH CAN

open end trimmed even with a hacksaw blade which has been ground to remove its set. In a short time three or four samples can easily be taken at increasing depths as desired to about 18 inches. For deeper samples, it would be necessary to dig a pit.

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[3] The containers can be obtained from Central Scientific Company, Chicago, Illinois, and are listed in their catalog J-141 as "tinned iron boxes," Cat. #10960, Size H.

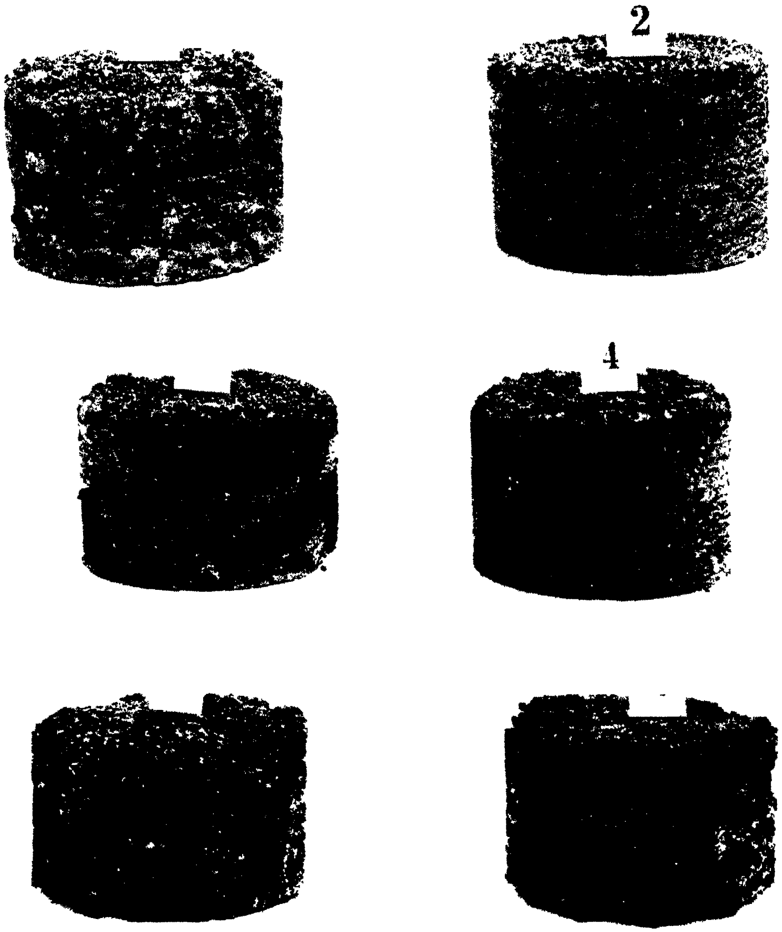

FIG. 3. EFFECT OF COMPACTION AND MOISTURE ON SOIL CORES OBTAINED BY DIFFERENT SAMPLING METHODS

Odd-numbered cores pushed; even-numbered, hammered. Cores 1 and 2 from compact wet soil; cores 3 and 4 from compact, dry soil; and cores 5 and 6 from loose wet soil. Note wall disturbance in cores 1, 3, and 6.

COMPARATIVE TESTS OF SAMPLERS

The new hammer-driven modification of the Lutz core-sampler was first tested in comparison with the original hand-push model in Cecil clay and Davidson loam. Where the two samplers failed to give about the same results for volume weights, a large core (17,200 cc.) was taken with a weighted jack to check which was the most accurate. Since the Lutz sampler and the hammer-driven modification differed both as to sample size and method of sampling, further tests were made to compare them for hammering and pushing methods at various initial states of soil compaction and moisture content in Cecil clay. In the order given, these comparative tests for the two samplers will be described and the results discussed.

Two soils, Cecil clay and Davidson loam, in the bins at the U. S. Department of Agriculture Tillage Machinery Laboratory at Auburn, Alabama, were fitted as for tillage tests with the soil at each depth in the bins very close to uniform volume weight. Eight samples were taken in the Cecil clay at two depths (sample centers, 5¼ and 9¼ inches deep) with both a hand-pressure (Lutz) and a sliding-hammer sampler. An accurate check on the average volume weight was made by using a large core-sampling cylinder with a sharp cutting edge beveled to take cores with very little distrubance. The cylinder was 12 inches in diameter and 9 inches high, having a volume of 17,200 cc. This was carefully jacked into the soil, spaded free, trimmed, and the procedure repeated to obtain three samples from the 3- to 12-inch depth range. No compression or disturbance of these large cores was observed. Sixteen samples were taken with both hammer and hand-pressure samplers in the Davidson loam at the same average depth (sample centers, 9¼ inches deep).

The samples taken from the Cecil clay with the hammer sampler were much less variable and more nearly in agreement with the large check cores than the hand-pressure samples (table 1). Careful examination of the samples indicated that the 83-cc. cans in the hand-pushed sampler usually failed to fill completely even though the sampler rim was forced down flush with the soil surface. The soil appeared to be compressed downward away from the cutting edge so that an undisturbed core was not obtained.

The average results were about the same for the samples taken in Davidson loam. The average volume weight for the 16 cores taken by the Lutz sampler was 1.478 with a range of 0.24 between extremes. The average volume weight for those taken by the hammer sampler was 1.478 with a range of 0.20. Although the mean values obtained are essentially the same, the individual results varied less with the samples taken with the hammer. Apparently, a soil low in plastic colloids, such as the Davidson, can be sampled satisfactorily with either sampler. The slightly less variable results with the hammer sampler were probably due to the larger core volume (470 as compared with 83 cc.). There was no evidence of sample compression with this soil, even though the moisture, in most cases, was a little higher than the lower plastic limit (about 9 per cent).

Since the first study with Cecil clay did not differentiate the effects of core size and of sampling method, another test with this soil was made. The bin was uniformly fitted as before and then divided into two sections lengthwise. One was heavily and the other lightly compacted, and then the bin was thoroughly and uniformly wetted by a constant-speed sprinkler car. A sliding hammer was added to the upright pipe of the smaller (83-cc.) sampler, and one sample was taken by pushing and one by hammering with each sampler from the soil surface at ten different locations in each section. The first set of samples was taken when the soil was in a nearly saturated condition. Other sets were taken as the soil dried so as to get samples with moisture varying from very wet to dry in heavily and lightly compacted conditions. A preliminary check showed that with this preparation the mean volume weight of the soil varied very little with depth near the surface and such differences as occurred between 470-cc. and 83-cc. cores did not result from the small difference in sampling depth due to core height.

TABLE 1

Effect of sampler and of soil moisture on volume weights obtained for a uniformly prepared Cecil clay test bin soil

Effect of Sampler

MOISTURE RANGE	NUMBER OF SAMPLES			MEAN VOLUME WEIGHT				VALUE OF t†
	Pushed 83 cc.	Hammered 470 cc.	Jacked 17,200 cc.	Hammered, 470 cc.	Pushed, 83 cc.	Jacked 17,200 cc.	Difference	
per cent								
25–29	8	8	—	1.200	1.079	—	+.121	5.99**
29–31	8	8	—	1.236	1.070	—	+.166	3.40*
25–29	8	—	3	1.200	—	1.187	+.013	0.78
25–29	—	8	3	—	1.079	1.187	+.108	2.75*

Effect of Soil Moisture

SAMPLER	NUMBER OF SAMPLES	MEAN VOLUME WEIGHT			VALUE OF t
		25–29 per cent Moisture	29–31 per cent Moisture	Difference	
Hammered, 470 cc.	8	1.200	1.236	−.036	0.78
Pushed, 83 cc.	8	1.079	1.070	+.009	0.177

† Fisher's value for estimating probability and denoting significance (4, p. 65).

* Significant ($P < .05$; $P > .01$).

** Highly significant ($P < .01$).

The results for the heavily compacted soil are shown in table 2 and those for the lightly compacted condition in table 3. In cases where the soil moisture content for any two sets of samples differed very little, these were averaged for moisture percentage and volume weights as single groups in the analysis of the data. With the heavily compacted soil the method of hammering consistently resulted in cores of higher volume weight than for pushing. Likewise the 470-cc. cores were greater in volume weight than the 83-cc. cores. It appears that the difference between methods resulted from a greater disturbance of the core wall with pushing than with hammering (fig. 3). Also, the 83-cc. cores failed to fill the cans as well as the 470-cc. cores because of the greater wall-surface resistance relative to the core diameter. A very small core would tend to plug the open end of the container, diverting the force intended for cutting

TABLE 2

Effect of soil moisture, core size, and sampling method upon volume weights obtained for heavily compacted Cecil clay

Effect of Sampling Method

MOISTURE RANGE	NUMBER OF SAMPLES		MEAN VOLUME WEIGHT			VALUE OF t
	Hammered	Pushed	Hammered	Pushed	Difference	
			Large cores			
29–25	20	20	1.308	1.256	+.052	7.60†
26–23	10	10	1.308	1.291	+.017	2.14*
23–21	10	5	1.337	1.316	+.013	1.00
19–17	10	5	1.337	1.284	+.053	2.40*
26–17	20	20	1.366	1.296	+.070	4.34†
			Small cores			
29–25	20	20	1.298	1.242	+.056	10.37†
26–23	10	10	1.260	1.231	+.029	1.96
23–21	10	10	1.292	1.254	+.038	3.31†
19–17	10	5	1.288	1.264	+.024	1.43
26–17	25	25	1.277	1.247	+.030	3.70†

Effect of Core Size

MOISTURE RANGE	NUMBER OF SAMPLES		MEAN VOLUME WEIGHT			
	Large cores	Small cores	Large cores	Small cores	Difference	
			Hammered			
29–25	20	20	1.308	1.298	+.010	1.77
26–23	10	10	1.308	1.260	+.048	3.46†
23–21	10	10	1.337	1.292	+.045	3.87†
19–17	10	10	1.337	1.288	+.049	3.58†
			Pushed			
29–25	20	20	1.256	1.242	+.014	2.10*
26–23	10	10	1.291	1.231	+.060	4.36†
23–21	5	10	1.316	1.254	+.062	2.98*
19–17	5	5	1.284	1.264	+.020	4.03†

* Significant ($P < .05; P > .01$).
† Highly significant ($P < .01$).

a sample free into that of compressing the soil downward and outward away from the mouth of the can. Hammering not only resulted in greater volume weights than pushing, but the differences were more pronounced in the very dry and the wet soil. In wet soil it was observed that hammering resulted in

TABLE 3

Effect of soil moisture, core size, and sampling method upon volume weights obtained for lightly compacted Cecil clay

MOISTURE RANGE	NO. SAMPLES	MEAN VOLUME WEIGHT			VALUE OF *t*
		Hammered	Pushed	Difference	
Large cores					
%					
34–27	10	0.983	1.017	−0.34	3.70†
28–26	10	1.008	1.024	−0.16	1.97
26–24	10	1.031	1.035	−0.004	0.37
23–18	30	1.068	1.048	+0.20	3.16†
Small cores					
34–27	10	0.969	1.001	−0.32	2.16†
28–26	10	0.953	0.980	−0.27	2.01
26–24	10	1.008	0.999	+.009	0.69
23–18	30	1.029	0.992	+.037	5.25†
Combined large and small cores					
28–26	20	0.980	1.002	−.022	2.59*

Effect of Core Size

MOISTURE RANGE	NO. SAMPLES	MEAN VOLUME WEIGHT			VALUE OF *t*
		Large cores	Small cores	Difference	
Hammered					
%					
34–27	10	0.983	0.969	+.014	1.09
28–26	10	1.008	0.953	+.045	4.38†
26–24	10	1.031	1.008	+.023	1.93
23–18	30	1.068	1.029	+.039	5.31†
Pushed					
34–27	10	1.017	1.001	+.016	1.46
28–26	10	1.024	0.980	+.044	4.67†
26–24	10	1.035	0.999	+.036	2.95†
23–18	30	1.048	0.992	+.056	7.88†
Combined hammered and pushed					
34–27	20	1.000	0.985	+.015	1.75
26–24	30	1.033	1.003	+.030	5.92†

* Significant ($P<.05$; $P>.01$).

† Highly significant ($P<.01$).

cutting freely into the soil, whereas pushing allowed the soil to adhere to the sampler. From the appearance of the cores it was clear that pushing caused disturbance due to adherence of the moist soil to the can wall (fig. 3). With dry soil the slight rocking and turning needed to force the sampler into the soil caused some fracturing and yielded cores slightly elliptical rather than round in cross section, thus reducing the volume weights.

From the very wet, lightly compacted soil, cores taken by hammering were somewhat lower in volume weight than those taken by pushing. Examination of these cores (fig. 3) indicates serious wall disturbance. It seems that a relatively loose soil when wet will be disturbed by the impact of the hammer, causing the particles and aggregates to settle and stick to the can wall and forming a wet sticky plug which resists filling and compacts the soil below the cutting edge so that a lighter core is taken by hammering than by pushing under these conditions. On the other hand, heavier cores were taken by hammering than by pushing from lightly compacted dry soil. This may have been due in part to the tendency of loose dry soil to settle more under the impact of the hammer than with the pressure due to pushing. As with the heavily compacted soil, the 83-cc. cores were lower in volume weight than the 470-cc. cores. This was more noticeable with dry than wet soil. It is conceivable that a wet aggregate will be readily cut, whereas a dry one will tend to be deflected by the cutting edge of the can. As the diameter of the can is decreased, the relative tendency to deflect outward rather than inward will increase. Thus, not only do small cores tend to give lower volume-weight values than large cores, but the effect increases as the soil dries.

It should be noted here that not all the change in mean volume weights with varying moisture is due to varying disturbance of the cores. As a result of shrinkage with drying, the cores should be more dense when taken dry than wet. At about 24 per cent moisture the soil cracked somewhat as a result of shrinkage. To avoid serious variation, care was taken to sample between the cracks. Hence, the small increase in the volume weight of the samples taken by hammering from the heavily compacted soil as the moisture changed from 25 to 23 per cent may be largely due to shrinkage. In the lightly compacted soil, it seems that the change with pushing was mostly due to shrinkage, whereas that with hammering was due somewhat to the different types of disturbance in loose wet and loose dry soil.

Apparently, for routine soil-core sampling, larger cores than those taken with the small Lutz tool would be better. The method to be used, whether by pushing or hammering, should be determined by soil conditions. Where the soil is loose, pushing appears to be more satisfactory as well as easier. With compact soil, hammering is more satisfactory. Thus one might follow the simple rule of using the method that is easier. As sampling is usually done in soil that is settled firmly and is below field-capacity moisture, the hammering method would ordinarily be more desirable. Baver (1) mentioned the shattering effect of the hammer. More disturbance due to the twisting and turning needed to push a sampler into dry, hard soil was observed than that due to the hammer. Also, disturbing effects usually result in taking lighter rather than heavier cores.

The increase in the size of the core taken and the addition of a sliding hammer has increased the usefulness of the Lutz-type sampler. Samples taken in the spring of 1949 in the field in a compact, though moist, Decatur clay subsoil with the original tool were seriously ruptured. It was impossible to force the sampler into the soil without turning it to some extent. During the summer the larger, sliding hammer sampler was used in the same field when the soil was too hard and dry to sample with a push-type sampler. Satisfactory cores were taken from the subsoil with the hammer sampler though there were occasional failures due to crumpling of the can edge as it was driven into the soil. For soil conditions where core samples are usually taken, the sliding hammer sampler is satisfactory.

CONCLUSIONS

The hand-pressure type of soil-core sampler failed to obtain cores free from disturbance in a clay soil but compared favorably with the hammer sampler in moist loam.

The sliding-hammer tool developed as a modification of the Lutz core sampler appears satisfactory for sampling most soils exclusive of those that are stony or extremely hard and compact.

The cores taken are of a convenient size (470-cc.) and large enough greatly to reduce sampling error and variation in results for replicates over the somewhat smaller cores taken by the Lutz sampler.

The tool is convenient to use in the field and experimental plots for sampling to depths of less than about 18 inches.

There is no need for sharpening or replacing damaged cutting heads, since the container edges are sharp enough to cut into the soil. In case of damage, a container is cheap and can be replaced by another numbered can.

Whether a sample should be taken by pushing or hammering is determined by soil conditions. Generally in loose very wet or very dry soil, where a sample can be obtained easily, pushing will cause less disturbance than hammering. In compact soils the reverse is true.

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APPLICATION OF CENTRIFUGAL FORCE TO OBTAIN A SATURATION EXTRACT OF SOIL SUITABLE FOR FLAME PHOTOMETRIC ANALYSIS[1]

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In connection with a study of the properties of a number of western Nebraska soils taken from sugar beet fields, several difficulties were encountered in obtaining clear saturation extracts for flame photometric analysis. Following the published procedure of the U. S. Regional Salinity Laboratory[2], involving the use of Büchner funnels with vacuum filtration, saturation extracts were obtained which were turbid with soil particles and therefore undesirable for use with the flame photometer. In addition, the technique was rather laborious and time-consuming. Richards[3] has recently described a plastic filter funnel apparatus which is said to require less care and time to obtain saturation extracts than the Büchner funnel.

METHOD OF OBTAINING SOIL EXTRACTS

Saturation extracts of a number of soils were obtained by centrifuging their pastes, which were prepared according to the procedure of the U. S. Regional Salinity Laboratory. The soil pastes were centrifuged at 2,400 revolutions per minute for 10 minutes in an International size 1, type S. B. centrifuge. Each of the extracts was then filtered in the following manner: Gooch crucibles were fitted with discs of filter paper and were placed under suction. A drop of the extract that separated from the soil paste during centrifuging was withdrawn with a dropping pipette and placed on top of each filter paper disc in such a manner that the paper was wetted and pressed firmly into place to prevent the soil colloids from passing around the edges of the paper. The remainder of the soil extract was decanted from the celluloid centrifuge tubes, poured through filters, and collected in clean, dry test tubes inside the filter flasks. The saturation extracts obtained in this manner were clear and free of colloids.

With some soils, depending upon the nature of the material and adsorbed ions, it may not be possible to obtain clear saturation extracts at comparatively low centrifuge speeds. In such cases, higher speeds should be used. Speeds as high as 11,500 revolutions per minute in an angle-head type centrifuge have been used to obtain the saturation extracts of soils.

RESULTS AND DISCUSSION

The results showing the recovery of saturation extracts as obtained by centrifugation at 2,400 revolutions per minute are presented in table 1. With 15 soil samples varying in moisture equivalent from 12.7 to 26.5 per cent, the recovery of saturation extracts obtained by centrifugation ranged from 24.0 to 33.8 per cent. The average recovery was 29.5 per cent. There was no relationship between the extract recovery percentages and the moisture-equivalent values of the samples.

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[1] Contribution from the department of agronomy, Nebraska Agricultural Experiment Station, Lincoln 1, Paper No. 488, Journal Series.

[2] U. S. Regional Salinity Laboratory. Diagnosis and improvement of saline and alkali soils. By laboratory staff, L. A. Richards, editor. 1947 (Multilithed.)

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To establish the magnitude of possible evaporation losses during centrifugation, measured volumes of distilled water were centrifuged under the same conditions as those under which the extracts were obtained. There were no measurable losses by evaporation under these conditions.

In carrying out the centrifugation technique, it is important to use celluloid or plastic centrifuge tubes, since glass tubes break.

TABLE 1

Recovery of the saturation extract of some western Nebraska soils by centrifugation

SOIL SAMPLE	WEIGHT OF SAMPLE	MOISTURE EQUIVALENT	WATER ADDED TO FORM SOIL PASTE	EXTRACT RECOVERED	
	gm.	*%*	*ml.*	*ml.*	*per cent*
1	200	19.4	84.3	26.5	31.4
2	200	16.0	68.1	19.0	27.9
3	200	16.2	73.3	18.5	25.2
4	200	22.8	80.7	24.0	29.7
5	200	21.0	74.1	21.0	28.3
6	200	14.0	66.0	18.5	28.0
7	200	12.7	75.0	18.0	24.0
8	100	19.1	41.6	13.0	31.2
9	120	15.4	43.0	13.0	30.2
10	200	25.1	84.3	28.5	33.8
11	200	20.0	81.4	24.0	29.5
12	200	15.3	81.0	25.0	30.9
13	200	22.0	81.5	26.0	31.9
14	200	26.5	86.2	26.0	30.2
15	200	25.0	84.1	25.5	30.3

SUMMARY

A method of obtaining the saturation extract of soils by means of centrifugation is described. An average recovery of 29.5 per cent of the water used to prepare soil pastes of 15 samples from western Nebraska was obtained with this technique. The centrifuged extracts were filtered to remove the soil particles that washed from the sides of the tubes during decantation.

The centrifugation method described is very easily carried out and involves only the simplest types of equipment generally found in soil laboratories. Comparatively low centrifuge speeds are sufficient for most soils. If, however, the soil material is highly colloidal or dispersed, the latter being dependent on the nature of the adsorbed ions, higher centrifuge speeds may be needed to obtain clear separations. The extracts obtained, being free of colloids, are well suited for flame photometric or other types of analyses.

Agricultural Chemistry. Edited by DONALD E. H. FREAR. D. Van Nostrand Company, Inc., New York, 1950. Pp. 812, figs. 72. Price $9.

This is the first of a 2-volume set to be known as "Principles of Agricultural Chemistry"—a modernized version of Liebig's "Organic Chemistry in Its Application to Agriculture and Physiology." It is divided into five parts: fundamental materials and processes, chemical processes, and plant, animal, and soil chemistry. Among the topics discussed are: the general chemistry of carbohydrates, lipids, amino acids, and enzymes; oxidations, cell chemistry, metabolism, absorption of inorganic substances, chlorophylls, pigments, utilization of carbohydrates and nitrogen, and hormones in plants; carbohydrate, lipid, and protein metabolism, digestion, absorption, and utilization of inorganic substances, and vitamins in animals; and minerals, colloids, and organic matter in soils. The 22 authors are specialists in the several fields of research. A list of 100 or more references is appended to each chapter. The editor is to be congratulated on having assembled such a wealth of useful material in one volume, which is destined to fill a highly important place on the reference shelves of the agricultural chemists of this country.

Isotopic Tracers and Nuclear Radiations with Applications to Biology and Medicine. By WILLIAM E. SIRI. McGraw-Hill Book Company, Inc., New York, 1949. Pp. 653, figs. 136. Price $12.50.

The author of this book has endeavored to present a simplified statement of the theory, methods, and principles involved in the use of isotopic tracers, with special reference to biology and medicine. The first part of the book deals with nuclei, gamma rays, beta and alpha particles, neutrons, fission, and radioactivity. The second part discusses mass spectrographs, Geiger counters, theory of tracer methods, handling of radioactive materials, the cyclotron, and a considerable number of other pertinent subjects. The third part deals with the applications in the study of plants and animals. The final chapter is an extended bibliography of more than 2,000 papers dealing with the general phases of the subject and with 57 individual elements. The illustrations are excellent, and the method of presentation is such as to permit of an understanding of the subject by those who are not necessarily specialists in mathematics and physics. This is a very useful book and should be at hand in every laboratory which is engaged in the study of isotopic tracers.

Louis Pasteur. By RENE J. DUBOS. Little, Brown and Company, Boston, 1950. Pp. 418. Price $5.

This is the type of book that every young scientist should read and reread. It holds up to plain view the obstacles to progress in the scientific field and the great rewards in accomplishment that accrue to the strong-minded man who is prepared to fight his way through, come what may. Chapter 13, dealing with mechanisms of discoveries, is one of the most interesting. It reveals how the mind of the genius in research works. It has to do not only with Pasteur, but with Tyndall, Lord Kelvin, Kekule, Darwin, Faraday, and many others who were able to look beyond the pale of ordinary man. Pasteur, "the most perfect man who has ever entered the kingdom of Science," went through poverty, personal losses, ill health, and fanatical opposition. But he continued to search for the truth and to marshall the necessary facts to prove his points. He was convinced that "Science and Peace will triumph over Ignorance and War." The author has made a highly important contribution to the history of this remarkable man. The illustrations, notably the photographs of Pasteur from youth to old age, are impressive.

Man on the Landscape. By VERNON GILL CARTER. National Wildlife Federation, Washington, D. C., 1949. Pp. 129, figs. 53. Price $1.50.

The purpose of this book is to serve the cause of conservation education. It begins by raising a series of 27 questions, of which the first is: "What causes our streams to be muddy?" and the last is: "Why do we have rural slums?" The answer, it says, is "plant deficiency." It then proceeds to consider the establishment of plants *en masse*, to outline the problems arising from deficiencies in the quantity and quality of vegetation, to study the complex maze of plant relationships, to set forth the principles of landscape management, and to suggest how the nation's youth can be made aware of the important and necessary part played by vegetative cover. The book is well illustrated, mostly by showing the negative aspects of land management. One sometimes wonders what effect this continual display of eroded lands, impoverished landscapes, miserable-looking livestock, and generally depressive scenes must have on the boys and girls of this country. It would seem that there might well be many advantages in the opposite angle of approach.

Out of My Later Years. By ALBERT EINSTEIN. Philosophical Library, New York, 1950. Pp. 282. Price $4.75.

Although one chapter in this book deals with the derivation of the equation $E=MC^2$, most of it has to do with matters of more concern to the author. The book is made up of 60 addresses, book prefaces, magazine articles, radio talks, and miscellaneous presentations covering the period from 1934 to 1950. Eight of these deal with science. The others are concerned with beliefs, public affairs, life itself, personalities, and Jews. Apparently the author has had plenty of time to reflect on such matters as "knowledge of what *is* does not open the door directly to what *should be*"; "the path to genuine religiosity does not lie through the fear of life"; "the school has always been the most important means of transferring the wealth of tradition from one generation to the next"; "the whole of science is nothing more than a refinement of every day thinking"; "we should be on our guard not to overemphasize science and scientific methods when it is a question of human problems"; "the atom bomb has brought about the effect that all the people living in cities are threatened everywhere and constantly with sudden destruction"; "we shall be able to solve the problem when it will be clearly evident to all that there is no other, no cheaper way out of the present position"; and, finally, "I do not believe that under present circumstances passive resistance is an effective method." The book reflects so much thinking of interest to all of us that it is entitled to a wide reading, notably by students who are aiming toward a life of scientific endeavor.

The Population Upsurge in the United States. By JOSEPH S. DAVIS. Food Research Institute, Stanford University, Stanford, California, 1949. Pp. 92, charts 20. Price, paper-bound, $1.

This is No. 12 of the war-peace pamphlets of the Food Research Institute. It deals with population developments in this country and directs attention to "a remarkable upsurge of population in the United States, accompanied by radical changes in age composition and geographical distribution." It is the author's contention that the magnitude and significance of the changing picture are not fully appreciated. One has the impression from reading this pamphlet that we may ultimately have more people in this country than has generally been expected. In a supplemental statement, the author indicates that the United States, Canada, Australia, and New Zealand belong in a new group of countries in which a really substantial rate of population increase can, and probably will, be maintained by a combination of very low mortality, moderate fertility, and moderate immigration: "Normally, and I think probably, this group of countries in the year 2000 will show a higher percentage of the world's population than it did in 1940." The population experts, like all other groups of specialists, do not agree on their interpretations in their special field of research.

Salt, the Fifth Element. By GARNETT LAIDLAW ESKEW. J. B. Ferguson and Associates, Chicago, 1948. Pp. 239. Price $3.

Someone has estimated that the salts of the ocean have a sale value of over $2 billion billion at present prices, to say nothing of the value of the ocean water itself, once the salts have been removed. But modern salt is not sea salt, as this book clearly shows. After exploring the history of salt in the old world and the new, the author takes up the development of the Morton Salt Company, which operates in all the nation's major salt fields, and which has already celebrated its 100th anniversary. One of the surprising features about the production of salt for human consumption today is that every effort is made to purify it, when one would think it would be desirable to leave some of the mineral impurities in it. Thus the author points out that 17 elements are known to be essential to life, then he points out that salt, with iodine added, supplies only two of these elements. One might well ask: Why not use sea salt as such? The book is interesting and instructive and contains many fine illustrations, from both the ancient and the modern world.

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